



Mesoporous SBA-15 silica catalyst functionalized with phenylsulfonic acid groups (SBA-15-Ph-SO₃H) as a novel hydrophobic nanoreactor solid acid catalyst for one-pot three-component synthesis of 2H-indazolo[2,1-b]phthalazine-triones and triazolo[1,2-a]indazole-triones

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Abstract. Phenyl sulfonic acid functionalized mesoporous SBA-15 silica (SBA-15-Ph-SO₃H) was prepared through the silanization of activated mesoporous SBA-15 with diphenyldichlorosilane (DPCS) followed with silylation and sulfonation, which was characterized by XRD, FT-IR, nitrogen adsorption analyses, BET and TEM. The sulfonic groups anchored to the silica surface of the pore walls are resistant to leaching in organic and aqueous solutions under mild conditions. This catalyst is found to be a recyclable heterogeneous catalyst for the rapid and efficient synthesis of various 2H-indazolo[2,1-b]phthalazine-triones and triazolo[1,2-a]indazole-triones. Also, this silylated mesoporous material containing phenylsulfonic acid groups has stability of bonded sulfonic acid surfaces toward water than those found in silica sulfuric acid (SSA) and sulfonated SBA-15.

Keywords: Nanoreactor, 2H-indazolo[2,1-b]phthalazine-triones, Mesoporous material, Solid acid catalyst.

1. Introduction

In recent years, organically functionalized ordered Mesoporous silicas [1-4] with a tunable pore structure, high surface areas and tailored composition has received great attention with broad application ranging from adsorbent [5-8], gas separation [9], and catalysis [10-15] to biological uses [16]. Some properties of these materials are: mechanically stable structure, high surface area, and large, ordered pores with narrow size distribution of an inorganic backbone. This organic Mesoporous functionalization has been widely achieved by the grafting of functional groups. Ordered mesoporous silicas (OMSs), particularly SBA-15 between other silica materials, have relatively good hydrothermal stability, and possesses hexagonal arrays of uniform pores with high special surface area and large pore volume.

The direct synthesis involving co-condensation of siloxane and organosiloxane species in the presence of different templating surfactants has been shown to be a promising alternative to the grafting procedures [17-20]. The covalent attachment of sulfonic acid groups to the surface of silica derivatives, several types of solid sulfonic acids, based on ordered mesoporous silicas, have been created in recent years [21-31]. Silylation and direct synthesis procedures have been used for the preparation of these sulfonic functionalized silica-based materials.

The active sulfonic group is obtained post-synthetically by the oxidation of propanethiol groups previously anchored to the surface [17,24-30] or by sulfonation reactions [21,22,31]. Multi-component reactions (MCRs) have proven to be a valuable asset in organic and medicinal chemistry [32-34]. Such protocols can be used for drug design, and drug discovery because of their simplicity, efficiency, and high selectivity [35]. This environmentally friendly process can reduce the number of steps and synthesis of bioactive and complex

molecules should be facile, fast, and efficient with minimal workup in this methodology [36, 37]. The combination of solvent-free conditions with multi-component reaction has been shown to be a powerful strategy to yield complex molecular structures in few synthetic steps [38, 39].

Aza-containing heterocyclic compounds are widespread in nature, and their applications to pharmaceuticals, agrochemicals, and functional materials are becoming more and more important [40]. Among a large variety of *N*-containing heterocyclic compounds, those containing hydrazine moiety as 'fusion site' have received considerable attention because of their pharmacological properties and clinical applications [41]. Moreover, fused phthalazines and urazole derivatives were found to possess multiple biological activities, such as antimicrobial [42], anticonvulsant [43], antifungal [44], anticancer [45], hypolipidemic [46], and anti-inflammatory activities [47]. Nevertheless the development of new synthetic methods for the efficient preparation of heterocycles containing phthalazine and urazole ring fragment is an interesting challenge. Recently, several elegant multicomponent strategies for the synthesis of 2H-indazolo[2,1-b]phthalazine-triones and triazolo[1,2-a]indazole-triones by multi component reactions utilizing catalysts have been reported [48-61].

2. Experimental section

2.1. Preparation of SBA-15

All chemicals were purchased from Merck except Pluronic123 and metformin hydrochloride which were obtained from Aldrich. The synthesis of SBA-15 was performed according to reported procedure [64]. In short explanation For the SBA-15 synthesis, 4.0 g of Pluronic P123 was dissolved in 50 mL of water and stirred for 5 h at room temperature. The mixture was added to 120 mL of 2 M hydrochloric acid solution and remained for 2h. Then, 8.5 g of TEOS was added to that solution and stirred for 24 h at 35 °C. The mixture was then

aged at 80 °C for 24 h without stirring. After completion of the reaction, the solid products were filtered, washed with deionized water, and air-dried overnight. The P123 was removed thoroughly with hot ethanol/water (3:2) using a Soxhlet apparatus for 24h. It was dried in air at 100 °C for 3 days.

2.2. Preparation of SBA-15-Ph-SO₃H

To a reaction mixture of SBA-15 (1 g) in dry toluene (30 ml), dichlorodiphenylsilane (5 ml) was added and refluxed under N₂ atmosphere for 12 h. After completion of the reaction, the white solid materials were filtered off and washed with toluene, dichloromethane, and methanol, and then dried in an oven at 80 °C overnight to give *SBA-15-Ph*.

Phenyl-modified SBA-15 was dispersed in dry hexane (50 mL) under nitrogen and then trimethylsilylchloride (TMSC, 3 mL) was added to the dispersion and refluxed for 8 h. Then it was cold down to the room temperature, filtered and washed with hexane to get the trimethylsilylated phenyl-modified SBA-15. The dry white solid was soaked in the solution of ClSO₃H (0.6 mL) in dry CHCl₃ (20 mL) and the reactant was refluxing for 2 h. Then it was filtrated and washed with dry CHCl₃. The solid achieved during this process was dried in vacuum at 60 °C for 10 h to obtain SBA-15 functionalized with phenyl sulfonic acid groups (SBA-15-Ph-SO₃H). The sulfonic content (the number of H⁺) of the catalyst based on elemental analysis (CHNS) (C 12.3%, H 2.88%, S 8.12%), and titration with NaOH is estimated to be 2.45 mmol/g.

2.3. General procedure for the synthesis of 2H-indazolo[2,1-b]phthalazine-triones and triazolo[1,2-a]indazole-triones in the presence of SBA-15-Ph-SO₃H under solvent-free conditions

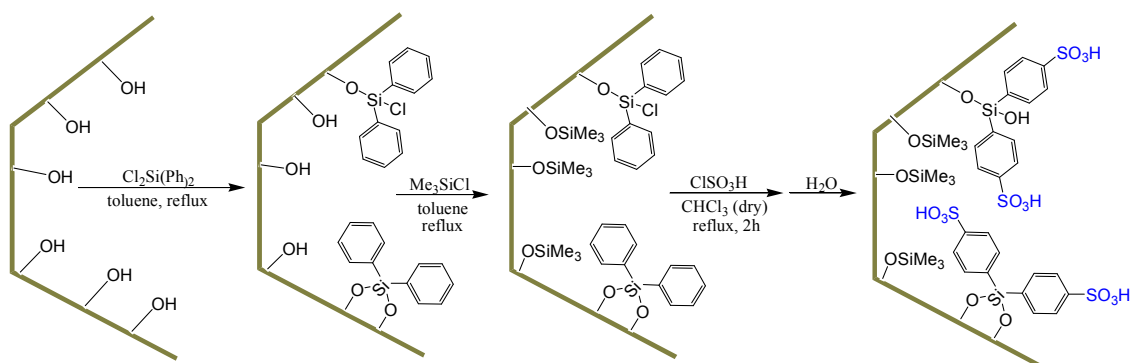
Phthalhydrazide or 4-phenylurazole (1 mmol), dimedone (1 mmol), aldehyde (1.1 mmol) and SBA-15-Ph-SO₃H (20 mg \approx 5 mol%,) were heated at 80 °C. The reactions were followed by thin layer chromatography (TLC) using hexane/ethyl acetate (3:1) as an eluent ($R_f=0.70$). After completion of the reaction, the mixture was washed with ethyl acetate and filtered to recover the catalyst. The filtrate was evaporated, and the crude product was recrystallized from EtOH/H₂O (4:1) to afford pure products. The desired pure products were characterized by comparison of their physical data with those of known compounds. In order to recover the catalyst, the solid was washed with ethanol, ethyl acetate and dried. The recovered catalyst was reused another time.

3. Results and discussion

3.1. Catalyst characterization

There has been considerable interest in the development of heterogeneous solid acid catalysts to avoid the use of traditional homogeneous acid catalytic systems (H₂SO₄, HF, AlCl₃, BF₃, ...) which present serious drawbacks including hazards in handling, corrosiveness, production of toxic waste, and difficulties in separation. In this context, we wish to report the preparation of SBA-15-Ph-SO₃H as a modified sulfonic acid and a novel hydrophobic nanoreactor solid acid catalyst. In the present work SBA-15 was modified to contain covalently bonded phenyl-sulfonic groups on the inside surface of the channels and provide the silica supported material with Brønsted acid properties. SBA-15 was synthesized according to a previously described method using Pluronic P123, as the templating agent [31]. The P123 was then removed thoroughly with hot ethanol/water (3:2) using a Soxhlet apparatus for 24h. Then activated mesoporous SBA-15 was reacted with diphenyldichlorosilane (DPCS) to introduced phenyl groups inside the channels. In continuation, before sulfonation with chlorosulfonic acid, the solid was reacted with

trimethylsilylchloride (TMSC) as powerful silylating agent, to trimethylsilylation of the surface hydroxyl groups of phenyl-modified SBA-15, to form trimethylsilyl phenyl modified SBA-15 (**3**). Subsequent treatment with chlorosulfonic acid afforded the final catalyst, SBA-15-Ph-SO₃H as new solid acid catalyst with more stability in the presence of moisture (Scheme 1).



Scheme 1. Preparation of SBA-15-Ph-SO₃H.

The mesoporous SBA-15 silica catalyst functionalized with phenylsulfonic acid groups (SBA-15-Ph-SO₃H) was conveniently synthesized from commercially available and cheap materials grafting on SBA-15. The formation of SBA-15-Ph-SO₃H was verified using CHN, FT-IR, UV-vis, BET, SEM, TEM and XRD. The pathways of SBA-15-Ph-SO₃H fabrication are shown in Scheme 1 that was confirmed by FT-IR (Fig 1). As it is seen in the curve **A**, the formation of SBA-15 structure is evidenced by the IR bands located at 3420 cm⁻¹ (ν_{as} O-H of silanols), 1088 cm⁻¹ (ν_{as} Si-O), 807 cm⁻¹ (ν_s Si-O), 467 cm⁻¹ (σ Si-O-Si) (ν represents stretching, σ bending, s symmetric, and as asymmetric vibration, Fig 1). The signals appeared at 3100 cm⁻¹ and 1508 cm⁻¹ (ν phenyl), 878 cm⁻¹ and 856 cm⁻¹ (σ phenyl) in curve **B** indicate the existence of phenyl ring and successful attachment of dichlorodiphenylsilane to the SBA-15. SBA-15-Ph-SO₃H exhibits additional diffraction peaks corresponding to sulfonic acid group in curve **C**. The characteristic peaks of sulfonic acid group are occurred at 1169 cm⁻¹ (ν SO₂) and 574 cm⁻¹ (ν S-O).

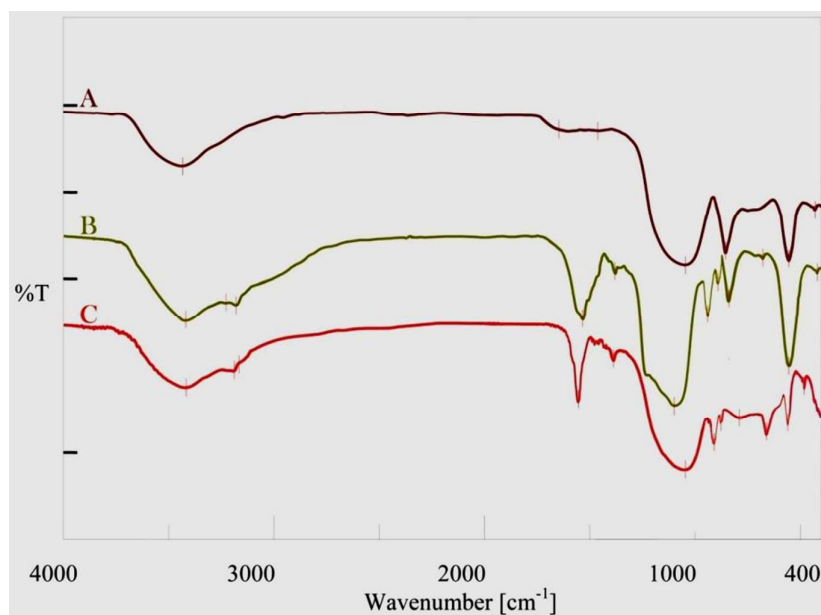


Fig. 1 FT-IR of the (A) SBA-15; (B) SBA-15-Ph; (C) SBA-15-Ph-SO₃H.

The sulfonic content (the number of H⁺) of the catalyst based on CHN analysis and titration with sodium hydroxide was estimated. In order to estimate the number of sulfonic group 60 mg SBA-15-Ph-SO₃H was added to a 25 mL aqueous solution of 1 M sodium chloride and was stirred for 72 h. Previous study indicated that heterogeneous acid titrations involve mass transfer limitations [32]. It seems that the presence of sodium chloride needs for property potentiometric titration. The addition of sodium chloride is required for enhancing the ion-exchange, facilitate the proton loss of the acid and the proton uptake of the base. While salts aid in improving the titration, their extensive addition leads to activities that deviate significantly from the actual proton concentrations. In this process ion exchange occurred between sulfonic acid protons and sodium ions. Then titration of this solution by NaOH (0.05 M) was carried out and the acid exchange capacity of catalyst was determined to be 2.45 mmol/g. This amount is different from the acquired results via CHN analysis (2.54 mmol/g) that can related to the limitation of titration regarding to heterogeneous acid.

The small-angle XRD patterns for SBA-15 and SBA-15-Ph-SO₃H are shown in Fig. 2. Three well-resolved diffraction peaks in the 2θ range of $0.8-2^\circ$ are observed for the SBA-15-Ph-SO₃H as an organic-inorganic hybrid material like to SBA-15 parent. However, the ordered structure of SBA-15-Ph-SO₃H remained intact, which was supported by XRD results. This patterns feature distinct Bragg peaks in the 2θ range of $0.8-2^\circ$, which can be indexed as (1 0 0), (1 1 0) and (2 0 0) reflections of a two-dimensional hexagonal structure of SBA-15 material. The present of these peaks indicates that the crystallographic ordering of the mesopores in SBA-15-Ph-SO₃H is retained after grafted. Also a noticeable change of SBA-15-Ph-SO₃H in the intensity ratios of these reflections (1 0 0), (1 1 0) and (2 0 0) was observed and they are lower than that of SBA-15, implying that the change of electron density contrast after grafting and distribution of scatters within the unit cell that affects the diffraction intensities.

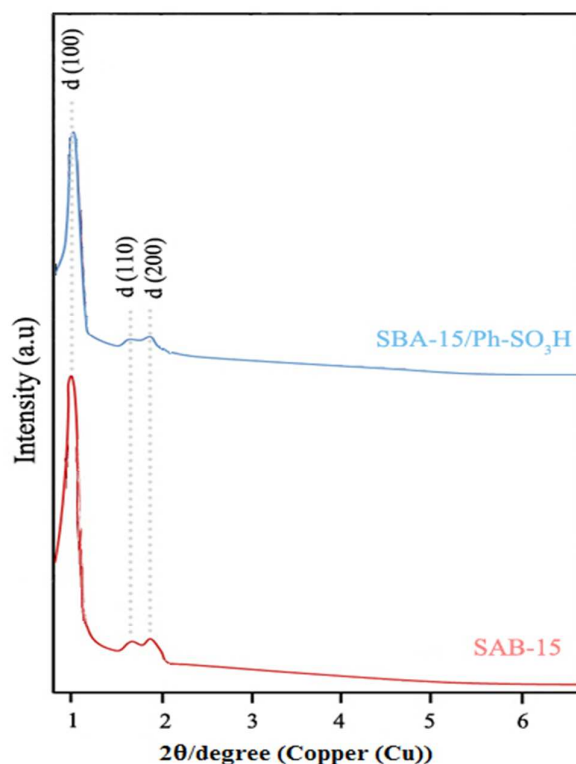


Fig. 2 XRD small angle patterns of the parent SBA-15 and SBA-15-Ph-SO₃H.

Nitrogen adsorption-desorption isotherms of SBA-15, SBA-15-Ph-SO₃H are shown in Fig. 3. The isotherms were all Type IV with a H1 hysteresis loop and a steep increase in adsorption at relative pressures of 0.6-0.8 for SBA-15 samples attributed to capillary nitrogen condensation according to IUPAC classification [62]. The BET surface area (S_{BET}), total pore volume (V_{BJH}), and mean pore diameter (MPD) of SBA-15 is 830 m²/g, 0.85 cm³/g, and 6.56 nm, respectively. Remarkably, after functionalization of SBA-15, the SBA-15-Ph-SO₃H carrier possesses a S_{BET} of 783 m²/g, V_{BJH} of 0.82 cm³/g, and a MPD of 5.94 nm. The S_{BET} , V_{BJH} and MPD of the modified support were significantly reduced compared to the parent SBA-15 (this decrease indicates the decrease in interaction between adsorbate, N₂ molecules, and the nano-sized SBA-15 surface after modification with organic groups). Therefore this observation confirmed that the organic groups prefer to be grafted in the ordered nanopores.

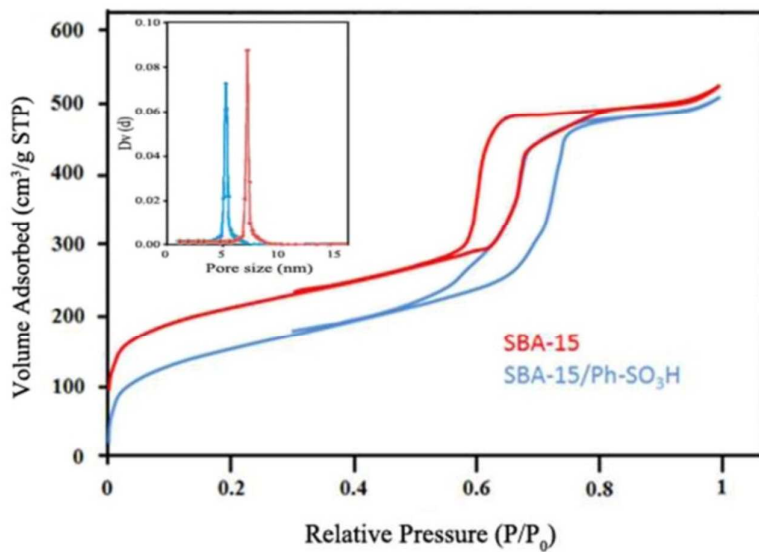


Fig. 3 Nitrogen adsorption-desorption profiles and pore size distribution of the SBA-15 and SBA-15- Ph-SO₃H.

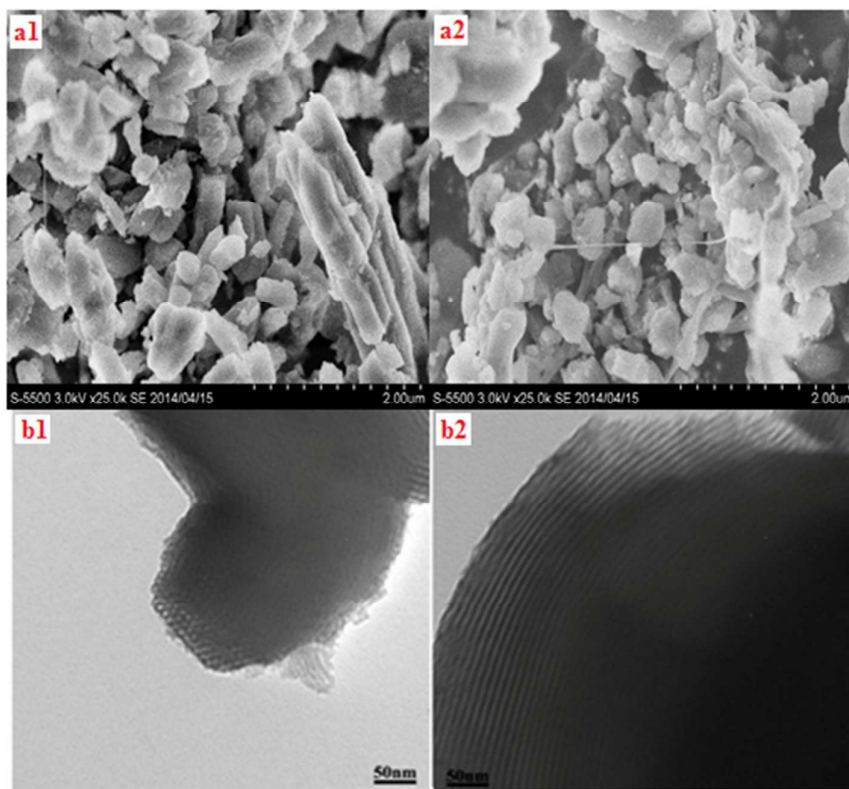
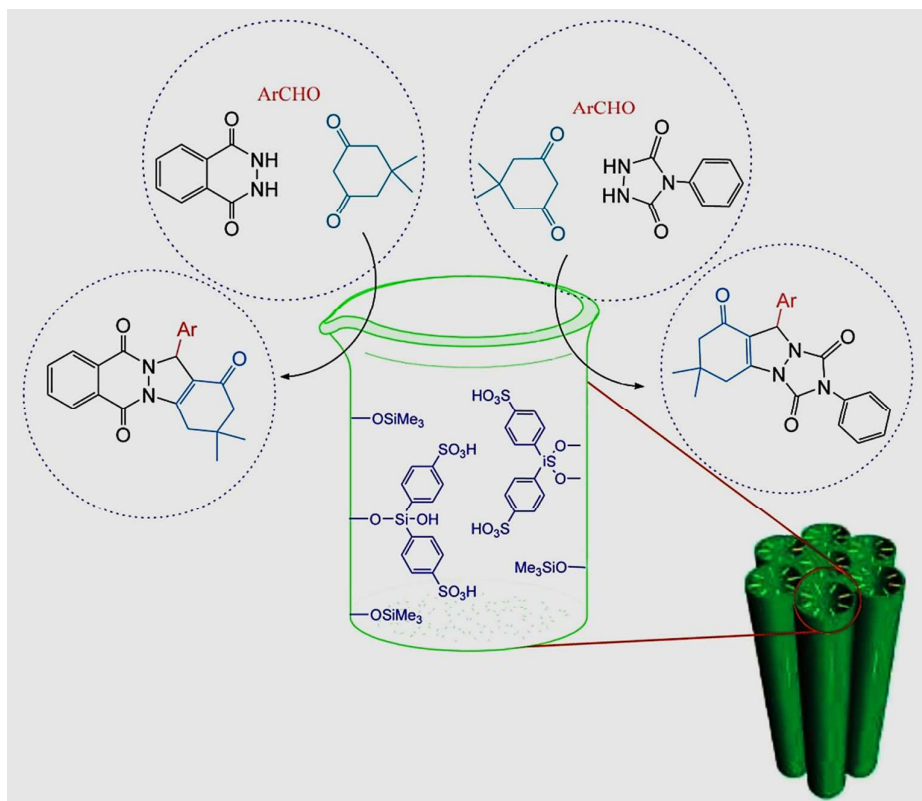


Fig. 4 TEM and SEM images of (a) SBA (b) SBA-15-Ph-SO₃H.

Furthermore, the structural elucidation of the SBA as a support and SBA-15-Ph-SO₃H was performed in some details using TEM and SEM techniques. SEM images of the catalysts (Fig. 4 a1, a2) show that the attachment of organic components to the SBA-15 materials has no distinct influence on the morphology of composition. TEM images of the catalyst (Fig. 4 b1, b2) show the ordered mesostructure in large domains and no distinct defect is observed.

3.2. Catalytic studies

In continuation of our interest in using the solid acid catalysts in organic transformations [63], herein we report the catalytic activity of phenylsulfonic acid modified mesoporous SBA-15 (SBA-15-Ph-SO₃H) as a novel nanoreactor solid acid catalyst for synthesis of 2H-indazolo[2,1-b]phthalazine-triones and triazolo[1,2-a]indazole-triones via the one-pot three-component reaction of dimedone, aldehydes with phthalazine or *N*-phenylurazoles under solvent-free conditions at 80 °C (Schemes 2).



Schemes 2. Synthesis of 2H-indazolo[2,1-b]phthalazine-triones and triazolo[1,2-a]indazole-triones.

In order to achieve optimum conditions, we initially investigated the reaction of phthalhydrazide (1.0 mmol), 3-nitrobenzaldehyde (1.1 mmol), and 5,5-dimethylcyclohexane-1,3-dione (1.0 mmol) in the presence of prepared catalyst in different conditions. Best result was obtained under solvent-free conditions in the presence of catalytic amount of SBA-15-Ph-SO₃H (5 mol%). The reaction afforded 96% of 3,4-dihydro-3,3-dimethyl-13-(3-nitrophenyl)-2Hindazolo[2,1-b] phthalazine-1,6,11(13H)-trione by a simple work-up after 5 min. In order to recognize the capability of the catalyst, the above reaction was repeated without catalyst under solvent free conditions. The reaction did not proceed even after prolonged reaction time and no desired product was formed which supported the catalytic activity of SBA-15-Ph-SO₃H.

The generality of this reaction was examined using different aromatic and aliphatic aldehydes. The reactions proceeded smoothly and equally well for electron-withdrawing as well as electron-donating substituents on aldehydes to afford the corresponding phthalazine-triones in good to excellent yields (Table 1, entries 1-9) and in very short reaction times. This method offers significant improvements with regard to the scope of the transformation, simplicity, and green aspects by avoiding expensive or corrosive catalysts.

Table 1
Synthesis of indazolo[2,1-b]phthalazine-triones in the presence of SBA-15-Ph-SO₃H.

Entry	Aldehyde	Time (min)	Yield (%) ^a	TOF (h ⁻¹) ^b	Mp (°C)	
					Found	Reported ^{lit.}
1	C ₆ H ₅	10	90	1.08	203-205	204-206 ⁴⁸
2	4-Cl-C ₆ H ₄	7	85	1.45	263-265	262-254 ⁵⁴
3	4-Br-C ₆ H ₄	5	95	2.29	264-266	265-267 ⁵⁵
4	4-MeO-C ₆ H ₄	5	96	2.31	217-219	218-220 ⁵⁵
5	3-NO ₂ -C ₆ H ₄	5	96	2.31	268-269	267-268 ⁵⁵
6	2,4-di-Cl-C ₆ H ₃	15	85	0.68	234-236	234-236 ⁵⁴
7	3,4,5-tri-MeO-C ₆ H ₂	10	95	1.15	187-189	188-190 ⁵⁸
8	Propanal	50	75	0.18	145-147	145-147 ⁵⁴
9	Butanal	45	80	0.21	135-137	136-138 ⁵⁴

^aIsolated yields

^bTOF, turnover frequencies.

Finally, to assess the present protocol with respect to other reported methods for the preparation of 3,4-dihydro-3,3-dimethyl-13-(3-nitrophenyl)-2Hindazolo[2,1-b] phthalazine-1,6,11(13H)-trione, the presented procedure by using SBA-15-Ph-SO₃H as catalyst was compared with other systems. From Table 2, it can be seen that present system gave higher conversions and yields compared to other reported systems.

Table 2

Comparison of the activity of different processes for the synthesis of 3,4-dihydro-3,3-dimethyl-13-(3-nitrophenyl)-2Hindazolo[2,1-b] phthalazine-1,6,11(13H)-trione.

Aldehyde	Catalyst	Reaction conditions	Yield (%)	Ref.
3-NO ₂ C ₆ H ₄ CHO	SBA-15-Ph-SO ₃ H	Solvent-free, 80 °C, 5 min	96	this study
	<i>N</i> -Bromosulfonamide	Solvent-free, 100 °C, 10 min	91	54
	PEG-OSO ₃ H	Solvent-free, 80 °C, 10 min	92	59
	[bmim]BF ₄	Solvent-free, 80 °C, 30 min	90	49
	Ce(SO ₄) ₂ .4H ₂ O	Solvent-free, 125 °C, 5 min	84	51

In the next step, the scope and efficiency of the prepared catalyst were explored under the optimized reaction conditions, for the condensation of *N*-phenyl urazoles with various aldehydes and dimedone to furnish the corresponding products (Scheme 1). The results are displayed in Table 3. As it can be seen the triazolo[1,2-a]indazole-trione derivatives were obtained in high yields and short reaction times.

Table 3

Synthesis of triazolo[1,2-a]indazole-triones in the presence of SBA-15-Ph-SO₃H.

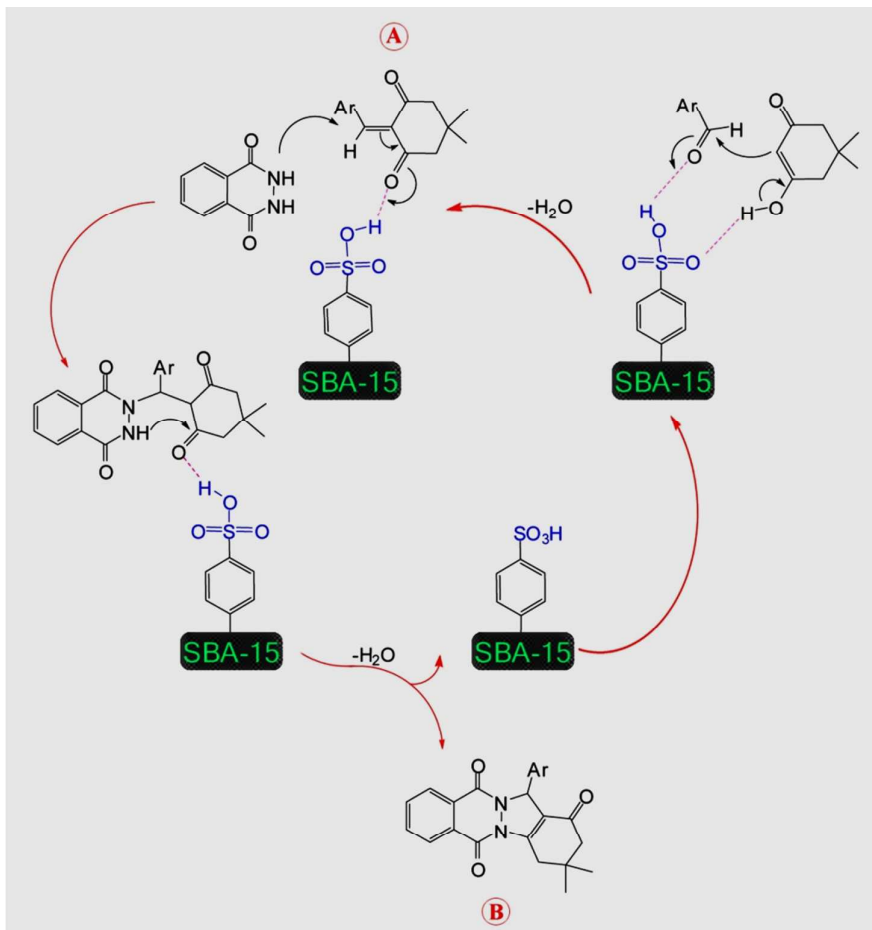
Entry	Aldehyde	Time (min)	Yield (%) ^a	TOF (h ⁻¹) ^b	Mp (°C)	
					Found	Reported ^{lit.}
1	C ₆ H ₅	30	92	0.37	189-191	190-192 ⁵⁷
2	4-Cl-C ₆ H ₄	40	95	0.29	170-172	166-168 ⁶¹
3	4-Br-C ₆ H ₄	30	95	0.38	185-187	185-187 ⁵⁷
4	4-Me-C ₆ H ₄	35	90	0.31	163-165	160-162 ⁶¹
5	3-NO ₂ -C ₆ H ₄	20	96	2.90	130-132	131-133 ⁵⁷
6	2-Cl-C ₆ H ₄	45	80	0.21	177-178	177-178 ⁵⁷

^aIsolated yields

^bTOF, turnover frequencies.

The formation of 2H-indazolo[1,2-b]phthalazine-trione derivatives in the presence of SBA-15-Ph-SO₃H, which should be synthetically useful and practical, as presented in Scheme 3. A plausible pathway involves initial a SBA-15-Ph-SO₃H catalyzed Knoevenagel

condensation of dimedone with aldehyde intermediate **A** was formed. Subsequent Michael addition of phthalhydrazide to intermediate **A** was occurred in the catalytic media, followed cyclization affords the corresponding product **B** in the catalytic cycle (Scheme 3).



Scheme 3. Proposed mechanism for the SBA-15-Ph-SO₃H-catalyzed synthesis of indazolo[2,1-b]phthalazine-triones.

3.3. Reusability of catalyst

The reusability of the catalyst in the reaction of 3-nitrobenzaldehyde, dimedone, and phthalhydrazide under solvent-free conditions at 80 °C in 5 minute was studied. In this procedure, after completion of each reaction, hot ethylacetate was added to the reaction mixture and was shaken for a few minutes to dissolve the product. The catalyst (insoluble in solvent) was filtered and washed with hot ethanol and ethylacetate, and dried. The recovered

catalyst was reused five times and smooth loss of catalytic activity was observed from the 5th time of reuse (Fig. 5).

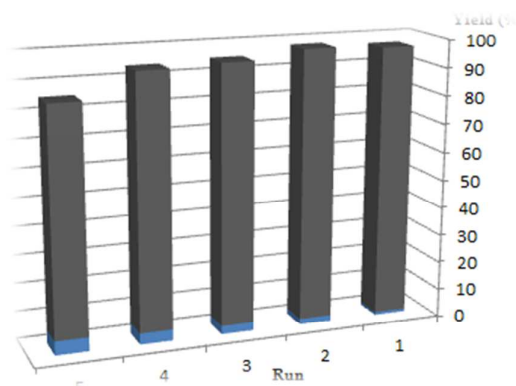


Fig. 5. The catalytic activity of SBA-15-Ph-SO₃H in five cycles for the reaction of 3-nitrobenzaldehyde, dimedone, phthalhydrazide.

The loss of catalytic activity for SBA-15-Ph-SO₃H may be due to that the catalyst channels could be filled by reactant molecules or products, and subsequently decreasing the catalytic activity.

3.4. Stability and leaching of catalyst

In another study, the stability and leaching of SBA-15-Ph-SO₃H is compared with silica sulfuric acid (SSA) and sulfonated SBA-15. We added 0.5 g of each catalyst in the separate column and then washed them with 20 mL water for 2 times recognize the stability and leaching of bonded sulfonic acid surfaces toward water. After washing, the pH value analysis of water shown that only the pH for our catalyst is unchanged [6,14]. This observation indicated that the stability of SBA-15-Ph-SO₃H as a solid acid heterogeneous nano catalyst toward water and hydrolysis condition. This stability may be because of steric and hydrophobic effects of phenyl groups in SBA-15-Ph-SO₃H toward water attack [19-33].

Our preliminary investigations demonstrate that catalyst SBA-15-Ph-SO₃H is very stable to air and moisture. The leaching and heterogeneous pathway inside the nanospace of the

prepared catalyst were tested for the reaction of phthalhydrazide (1.0 mmol), benzaldehyde (1.1 mmol), and 5,5-dimethylcyclohexane-1,3-dione (1.0 mmol) to afford of 3,4-dihydro-3,3-dimethyl-13-(phenyl)-2H-indazolo[2,1-b] phthalazine-1,6,11(13H)-trione under solvent-free conditions in the presence of nanoreactor. The reaction was quenched (by dilution with EtOAc) after 3 min and filtered off (~40% conversion). Next, EtOAc was evaporated, and the residue was then subjected to further heating under solvent-free conditions at 80 °C. We found that no further catalytic activity was observed upon heating for 3 h. Therefore, we may conclude that any sulfonic acid group that leaches into the reaction mixture are not active homogeneous catalysts and that the observed catalysis is truly heterogeneous in nature.

4. Conclusion

In conclusion, we have prepared phenyl sulfonic acid functionalized mesoporous SBA-15 silica (SBA-15-Ph-SO₃H) as a novel hydrophobic nanoreactor solid acid catalyst, which was characterized by XRD, FT-IR, nitrogen adsorption analyses, BET and TEM. The sulfonic groups anchored to the silica surface of the pore walls are resistant to leaching in organic and aqueous solutions under mild conditions. This catalyst is found to be a recyclable heterogeneous catalyst for the rapid and efficient synthesis of various 2H-indazolo[2,1-b]phthalazine-triones and triazolo[1,2-a]indazole-triones. Also, this silylated mesoporous material containing phenylsulfonic acid groups has stability of bonded sulfonic acid surfaces toward water than those found in silica sulfonic acid (SSA) and sulfonated SBA-15. Moreover, the catalyst has suitable hydrophobicity to drive out the water which is formed during the reaction from mesochannels.

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Graphical Abstract

Mesoporous SBA-15 silica catalyst functionalized with phenylsulfonic acid groups (SBA-15-Ph-SO₃H) as a novel hydrophob nanoreactor solid acid catalyst for one-pot three-component synthesis of 2H-indazolo[2,1-b]phthalazine-triones and triazolo[1,2-a]indazole-triones

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