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A mesoporous SBA-15 silica catalyst functionalized with phenylsulfonic acid groups (SBA-15-Ph-SO_3H) as a novel hydrophobic nanoreactor solid acid catalyst for a one-pot three-component synthesis of 2*H*-indazolo[2,1-*b*]phthalazine-triones and triazolo[1,2-*a*]indazole-triones

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Phenyl sulfonic acid functionalized mesoporous SBA-15 silica (SBA-15-Ph-SO_3H) was prepared through the silanization of activated mesoporous SBA-15 with diphenyldichlorosilane (DPCS) followed by silylation and sulfonation, and characterized by XRD, FT-IR, nitrogen adsorption analyses, BET theory and TEM. The sulfonic acid groups anchored to the silica surface of the pore walls were resistant to leaching in organic and aqueous solutions under mild conditions. This catalyst was found to be a recyclable heterogeneous catalyst for the rapid and efficient synthesis of various 2*H*-indazolo[2,1-*b*]phthalazine-triones and triazolo[1,2-*a*]indazole-triones. Also, this silylated mesoporous material containing phenylsulfonic acid groups has a greater stability of the sulfonic acid surface toward water than that of silica sulfuric acid (SSA) and sulfonated SBA-15.

1. Introduction

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

The direct synthesis involving the co-condensation of siloxane and organosiloxane species in the presence of different templating surfactants has been shown to be a promising alternative to grafting procedures.[17–20] By 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 acid functionalized silica-based materials.

The active sulfonic acid groups are 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 valuable assets 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 synthetic steps and the synthesis of bioactive and complex molecules should be facile, fast, and efficient with minimal workup using this methodology.[36,37] The combination of solvent-free conditions with a multi-component reaction has been shown to be a powerful strategy to yield complex molecular structures using few synthetic steps.[38,39]

Aza-containing heterocyclic compounds are widespread in nature, and their applications as pharmaceuticals, agrochemicals, and functional materials are becoming more and more important.[40] Among a large variety of N-containing heterocyclic compounds, those containing a hydrazine moiety at the 'fusion site' have received considerable attention because of their

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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 fragments is an interesting challenge. Recently, several elegant multicomponent strategies for the synthesis of 2*H*-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 a reported procedure.[64] As a short explanation of the SBA-15 synthesis, 4.0 g of Pluronic P123 was dissolved in 50 mL of water and was stirred for 5 h at room temperature. The mixture was added to 120 mL of 2 M hydrochloric acid solution and was left for 2 h. Then, 8.5 g of TEOS was added to the solution and was 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 a hot ethanol–water mixture (3 : 2) using a Soxhlet apparatus for 24 h. It was dried in air at 100 °C for 3 days.

2.2. Preparation of SBA-15-Ph-SO_3H

To a reaction mixture of SBA-15 (1 g) in dry toluene (30 mL), dichlorodiphenylsilane (5 mL) was added and refluxed under a N_2 atmosphere for 12 h. After completion of the reaction, the white solid material was filtered off and washed with toluene, dichloromethane, and methanol, and was 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 cooled down to room temperature, filtered and washed with hexane to get trimethylsilylated phenyl-modified SBA-15. The dry white solid was soaked in a solution of $ClSO_3H$ (0.6 mL) in dry $CHCl_3$ (20 mL) and was refluxed for 2 h. Then it was filtrated and washed with dry $CHCl_3$. The solid achieved during this process was dried under vacuum at 60 °C for 10 h to obtain SBA-15 functionalized with phenyl sulfonic acid groups (SBA-15-Ph-SO_3H). The sulfonic acid 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^{-1}.

2.3. General procedure for the synthesis of 2*H*-indazolo[2,1-*b*]phthalazine-triones and triazolo[1,2-*a*]indazole-triones in the presence of SBA-15-Ph-SO_3H under solvent-free conditions

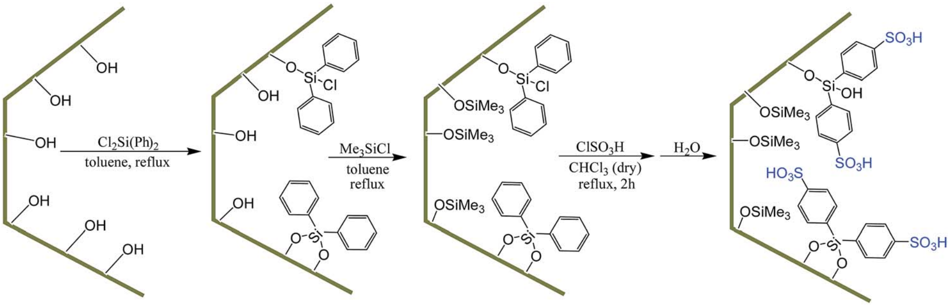
Phthalhydrazide or 4-phenylurazole (1 mmol), dimedone (1 mmol), aldehyde (1.1 mmol) and SBA-15-Ph-SO_3H (20 mg $\approx$ 5 mol%) were heated at 80 °C. The reaction was followed by thin layer chromatography (TLC) using hexane/ethyl acetate (3 : 1) as an eluent ($R_f = 0.70$). After completion of the reaction, 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–H_2O (4 : 1) to afford the pure products. The desired pure products were characterized by the 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 catalyst systems (H_2SO_4, HF, $AlCl_3$, BF_3,…) which present serious drawbacks including hazardous handling, corrosiveness, production of toxic waste, and difficulties in separation. In this context, we wish to report the preparation of SBA-15-Ph-SO_3H 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 phenylsulfonic acid groups on the inside surface of the channels and to provide the silica supported material with Brönsted 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 a hot ethanol–water mixture (3 : 2) using a Soxhlet apparatus for 24 h. Then the activated mesoporous SBA-15 was reacted with diphenyldichlorosilane (DPCS) to introduce phenyl groups to the inside of the channels. In continuation, before the sulfonation with chlorosulfonic acid, the solid was reacted with trimethylsilylchloride (TMSC) as a powerful silylating agent, for trimethylsilylation of the surface hydroxyl groups of the phenyl-modified SBA-15, to form trimethylsilyl phenyl modified SBA-15 (**3**). Subsequent treatment with chlorosulfonic acid afforded the final catalyst, SBA-15-Ph-SO_3H as a new solid acid catalyst with greater stability in the presence of moisture (Scheme 1).

The mesoporous SBA-15 silica catalyst functionalized with phenylsulfonic acid groups (SBA-15-Ph-SO_3H) was conveniently synthesized from commercially available and cheap materials grafted onto SBA-15. The formation of SBA-15-Ph-SO_3H was verified using CHN, FT-IR, UV-vis, BET theory, SEM, TEM and XRD studies. The pathway of SBA-15-Ph-SO_3H fabrication is shown in Scheme 1 and was confirmed by FT-IR (Fig. 1). As is seen from curve A, the formation of the 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 $_{as}$



Scheme 1 Preparation of SBA-15-Ph-SO_3H.

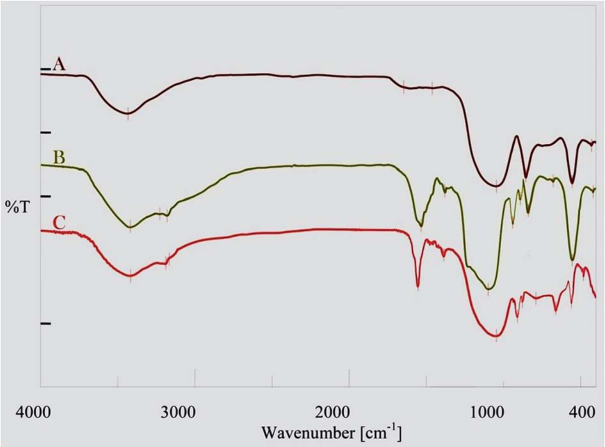


Fig. 1 FT-IR spectra of (A) SBA-15; (B) SBA-15-Ph; (C) SBA-15-Ph-SO_3H.

asymmetric vibrations, Fig. 1). The signals appearing 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 rings and the successful attachment of dichlorodiphenylsilane to SBA-15. SBA-15-Ph-SO_3H exhibits additional absorbance peaks corresponding to sulfonic acid groups in curve C. The characteristic peaks of the sulfonic acid groups occur at 1169 cm^{-1} (ν SO_2) and 574 cm^{-1} (ν S–O).

The sulfonic acid 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 acid groups, 60 mg of SBA-15-Ph-SO_3H was added to a 25 mL aqueous solution of 1 M sodium chloride and was stirred for 72 h. Previous studies have indicated that heterogeneous acid titrations involve mass transfer limitations.[32] It seems that the presence of sodium chloride is needed for a proper potentiometric titration. The addition of sodium chloride is required to enhance the ion-exchange, facilitating the proton loss of the acid and the proton uptake of the base. While the salt aids in improving the titration, the extensive addition leads to activities that deviate significantly from the actual proton concentration. In this process ion exchange occurred between the sulfonic acid protons and the sodium ions. Then titration of this solution with NaOH (0.05 M) was carried out and the acid exchange capacity of catalyst was determined to be 2.45 mmol g^{-1}. This amount is different from the results acquired *via* CHN analysis (2.54 mmol g^{-1}) which can be related to the limitation of the titration regarding the heterogeneous acid.

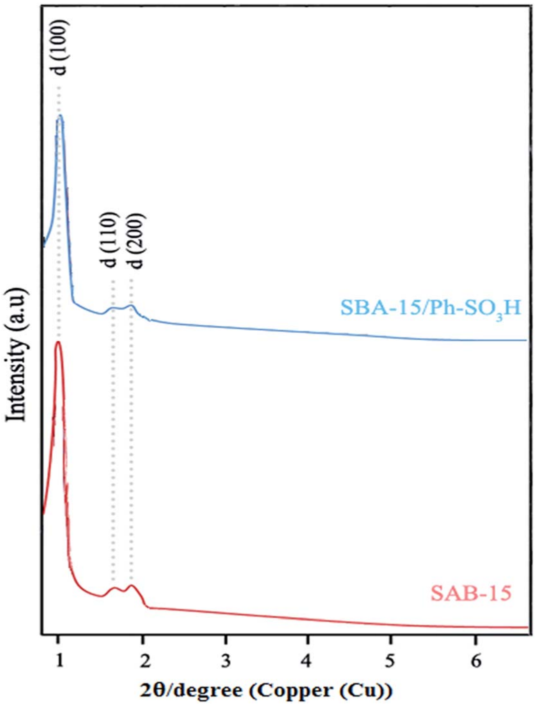


Fig. 2 XRD small angle patterns of the parent SBA-15 and SBA-15-Ph-SO_3H catalysts.

The small-angle XRD patterns of SBA-15 and SBA-15-Ph-SO_3H are shown in Fig. 2. Three well-resolved diffraction peaks in the 2θ range of 0.8–2° are observed for SBA-15-Ph-SO_3H as an organic–inorganic hybrid material similar to the SBA-15 parent. However, the ordered structure of SBA-15-Ph-SO_3H has remained intact, as supported by the XRD results. This pattern features distinct Bragg peaks in the 2θ range of 0.8–2°, which can be indexed as (1 0 0), (1 1 0) and (2 0 0) reflections of the two-dimensional hexagonal structure of the SBA-15 material. The presence of these peaks indicates that the crystallographic ordering of the mesopores in SBA-15-Ph-SO_3H is retained after grafting. Also a noticeable change for SBA-15-Ph-SO_3H in the intensity of these reflections (1 0 0), (1 1 0) and (2 0 0) was

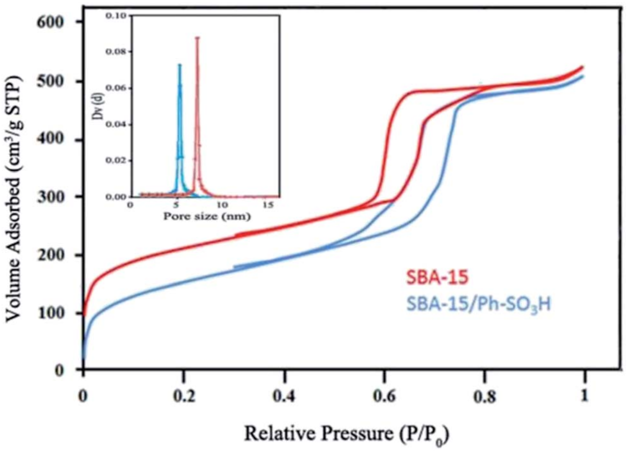


Fig. 3 Nitrogen adsorption–desorption profiles and pore size distribution of the SBA-15 and SBA-15-Ph-SO$_3$H catalysts.

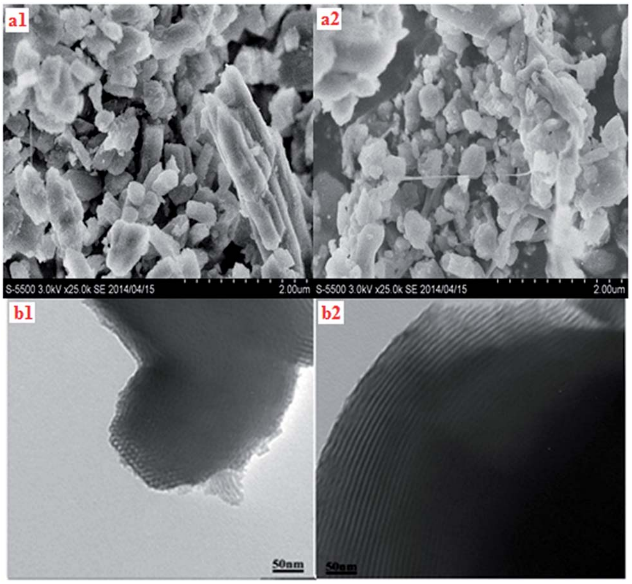


Fig. 4 (a) SEM and (b) TEM images of (1) SBA-15 and (2) SBA-15-Ph-SO$_3$H.

observed, they are lower than that of SBA-15, implying that the change in the electron density contrast after the grafting, changes the distribution of the scattering angles within the unit cell which affects the diffraction intensities.

The nitrogen adsorption–desorption isotherms of SBA-15 and SBA-15-Ph-SO$_3$H are shown in Fig. 3. The isotherms were both type IV with a H1 hysteresis loop and a steep increase in the adsorption at relative pressures of 0.6–0.8, for the SBA-15 sample this can be 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 were 830 m^2 g^{-1}, 0.85 cm^3 g^{-1}, and 6.56 nm, respectively. Remarkably, after functionalization of SBA-15, the SBA-15-Ph-SO$_3$H catalyst possessed a S_{BET} of 783 m^2 g^{-1}, V_{BJH} of 0.82 cm^3 g^{-1}, 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 a decrease in the interaction between the adsorbate, N$_2$ molecules, and the nano-sized SBA-15 surface after the modification with organic groups). Therefore this observation confirms that the organic groups prefer to be grafted in the ordered nanopores.

Furthermore, the structural elucidation of the SBA-15 and SBA-15-Ph-SO$_3$H catalytic supports was performed in some detail using TEM and SEM techniques. The SEM images of the catalysts (Fig. 4a1 and a2) show that the attachment of the organic components to the SBA-15 material has no distinct influence on the morphology of composition. The TEM images of the catalysts (Fig. 4b1 and b2) show the ordered mesostructure in large domains and no distinct defects are observed.

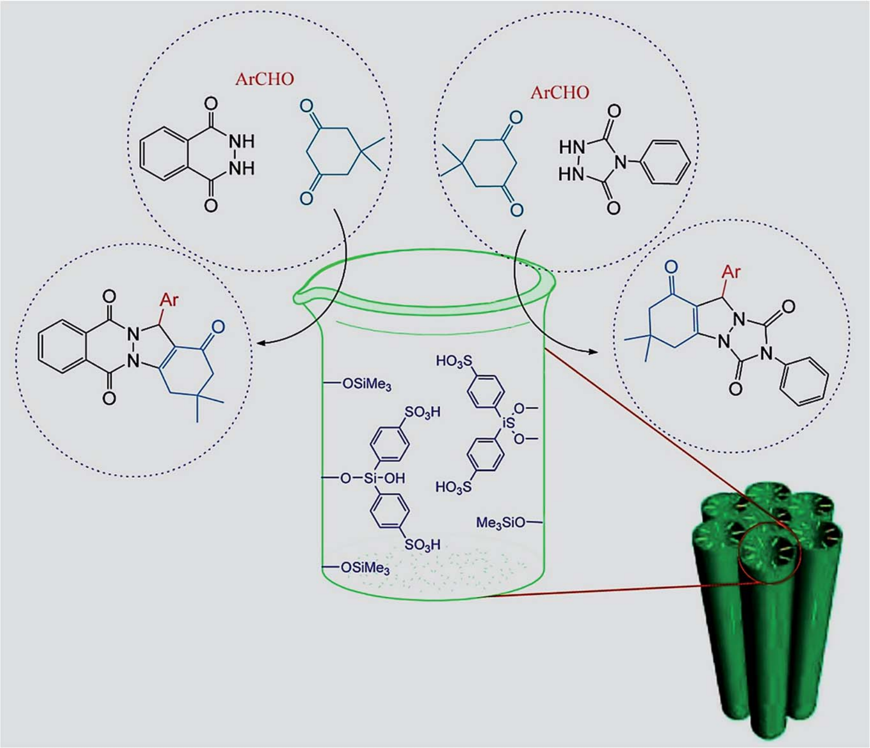
3.2. Catalytic studies

In a 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-SO$_3$H) as a novel nanoreactor solid acid catalyst for the synthesis of 2*H*-indazolo[2,1-*b*]phthalazine-triones and triazolo[1,2-*a*]indazole-triones *via* a one-pot three-component reaction of dimedone and aldehydes with phthalazine or *N*-phenylurazoles under solvent-free conditions at 80 °C (Scheme 2).

In order to achieve the 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 the prepared catalyst under different conditions. The best result was obtained under solvent-free conditions in the presence of a catalytic amount of SBA-15-Ph-SO$_3$H (5 mol%). The reaction afforded 96% of 3,4-dihydro-3,3-dimethyl-13-(3-nitrophenyl)-2*H*-indazolo[2,1-*b*]-phthalazine-1,6,11(13*H*)-trione by a simple work-up after 5 min. In order to deduce the capability of the catalyst, the above reaction was repeated without the catalyst under solvent free conditions. The reaction did not proceed even after a prolonged reaction time and no desired product was formed which supports the catalytic activity of SBA-15-Ph-SO$_3$H.

The generality of this reaction was examined by using different aromatic and aliphatic aldehydes. The reactions proceeded smoothly and equally well for electron-withdrawing as well as electron-donating substituents on the 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, the simplicity, and the green aspect by avoiding expensive or corrosive catalysts.

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)-2*H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-trione, the presented procedure using SBA-15-Ph-SO$_3$H as the catalyst was compared with other systems. From Table 2, it can be seen that the present system gave higher conversions and yields compared to the other reported systems.



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

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 can be seen the triazolo[1,2-*a*]indazole-trione derivatives were obtained in high yields and short reaction times.

The formation of the 2*H*-indazolo[1,2-*b*]phthalazine-trione derivatives in the presence of SBA-15-Ph-SO$_3$H, which should be synthetically useful and practical, is presented in Scheme 3. A plausible pathway involves an initial SBA-15-Ph-SO$_3$H catalyzed Knoevenagel condensation of dimedone with an aldehyde to form intermediate **A**. A subsequent Michael addition of phthalhydrazide to intermediate **A** occurred in the catalytic media, followed by cyclization to afford the corresponding product **B** in the catalytic cycle (Scheme 3).

3.3. Reusability of the catalyst

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

Table 1 Synthesis of indazolo[2,1-*b*]phthalazine-triones in the presence of SBA-15-Ph-SO$_3$H

Entry	Aldehyde	Time (min)	Yield[a] (%)	TOF[b] (h^{-1})	Mp (°C)	
					Found	Reported$^{lit.}$
1	C$_6$H$_5$	10	90	1.08	203–205	204–206 (ref. 48)
2	4-Cl–C$_6$H$_4$	7	85	1.45	263–265	262–254 (ref. 54)
3	4-Br–C$_6$H$_4$	5	95	2.29	264–266	265–267 (ref. 55)
4	4-MeO–C$_6$H$_4$	5	96	2.31	217–219	218–220 (ref. 55)
5	3-NO$_2$–C$_6$H$_4$	5	96	2.31	268–269	267–268 (ref. 55)
6	2,4-Di-Cl–C$_6$H$_3$	15	85	0.68	234–236	234–236 (ref. 54)
7	3,4,5-Tri-MeO–C$_6$H$_2$	10	95	1.15	187–189	188–190 (ref. 58)
8	Propanal	50	75	0.18	145–147	145–147 (ref. 54)
9	Butanal	45	80	0.21	135–137	136–138 (ref. 54)

[a] Isolated yields. [b] TOF, turnover frequencies.

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

Aldehyde	Catalyst	Reaction conditions	Yield (%)	Ref.
$3\text{-NO}_2\text{C}_6\text{H}_4\text{CHO}$	SBA-15-Ph-SO_3H	Solvent-free, 80 °C, 5 min	96	This study
	N-Bromosulfonamide	Solvent-free, 100 °C, 10 min	91	54
	PEG-OSO_3H	Solvent-free, 80 °C, 10 min	92	59
	$[\text{bmim}]\text{BF}_4$	Solvent-free, 80 °C, 30 min	90	49
	$\text{Ce(SO}_4)_2\cdot 4\text{H}_2\text{O}$	Solvent-free, 125 °C, 5 min	84	51

Table 3 Synthesis of triazolo[1,2-*a*]indazole-triones in the presence of SBA-15-Ph-SO_3H

					Mp (°C)	
Entry	Aldehyde	Time (min)	Yield[a] (%)	TOF[b] (h^{-1})	Found	Reported$^{\text{lit.}}$
1	C_6H_5	30	92	0.37	189–191	190–192 (ref. 57)
2	4-Cl–C_6H_4	40	95	0.29	170–172	166–168 (ref. 61)
3	4-Br–C_6H_4	30	95	0.38	185–187	185–187 (ref. 57)
4	4-Me–C_6H_4	35	90	0.31	163–165	160–162 (ref. 61)
5	3-NO_2–C_6H_4	20	96	2.90	130–132	131–133 (ref. 57)
6	2-Cl–C_6H_4	45	80	0.21	177–178	177–178 (ref. 57)

[a] Isolated yields. [b] TOF, turnover frequencies.

and a smooth loss of catalytic activity was observed from the 5th time of reuse (Fig. 5).

The loss of catalytic activity for SBA-15-Ph-SO_3H may be due to the catalyst channels being filled by reactant molecules or products, and subsequently decreasing the catalytic activity.

3.4. Stability and leaching of the catalyst

In another study, the stability and leaching of SBA-15-Ph-SO_3H were compared with silica sulfuric acid (SSA) and sulfonated SBA-15. We added 0.5 g of each catalyst to a separate column and then washed them with 20 mL of water 2 times to investigate the stability and leaching of the bonded sulfonic acid surfaces toward water. After washing, pH value analysis of the water showed that only the pH of our catalyst was unchanged.[6,14] This observation indicated the greater stability of SBA-15-Ph-SO_3H as a solid acid heterogeneous nano catalyst toward water and hydrolysis conditions. This stability may be because of the steric and hydrophobic effects of the phenyl groups in SBA-15-Ph-SO_3H toward water attack.[19–33]

Our preliminary investigations demonstrate that the catalyst SBA-15-Ph-SO_3H is very stable to air and moisture. The leaching and heterogeneous pathways 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 the 3,4-dihydro-3,3-dimethyl-13-(phenyl)-2*H*-indazolo[2,1-*b*]-phthalazine-1,6,11(13*H*)-trione under solvent-free conditions in the presence of a nanoreactor. The reaction was quenched (by dilution with EtOAc) after 3 min and filtered off (~40% conversion). Next, the 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 groups that leach 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-SO_3H) as a novel hydrophobic nanoreactor solid acid catalyst, which was characterized by XRD, FT-IR, nitrogen adsorption analyses, BET theory and TEM. The sulfonic acid groups anchored to the silica surface of the pore walls are resistant to leaching in organic and aqueous solutions under mild conditions. This catalyst was found to be a recyclable heterogeneous catalyst for the rapid and efficient synthesis of various 2*H*-indazolo[2,1-*b*]phthalazine-triones and triazolo[1,2-*a*]indazole-triones. Also, this silylated mesoporous material containing phenylsulfonic acid groups has a greater stability of the bonded sulfonic acid surface toward water than that of 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 the mesochannels.

Acknowledgements

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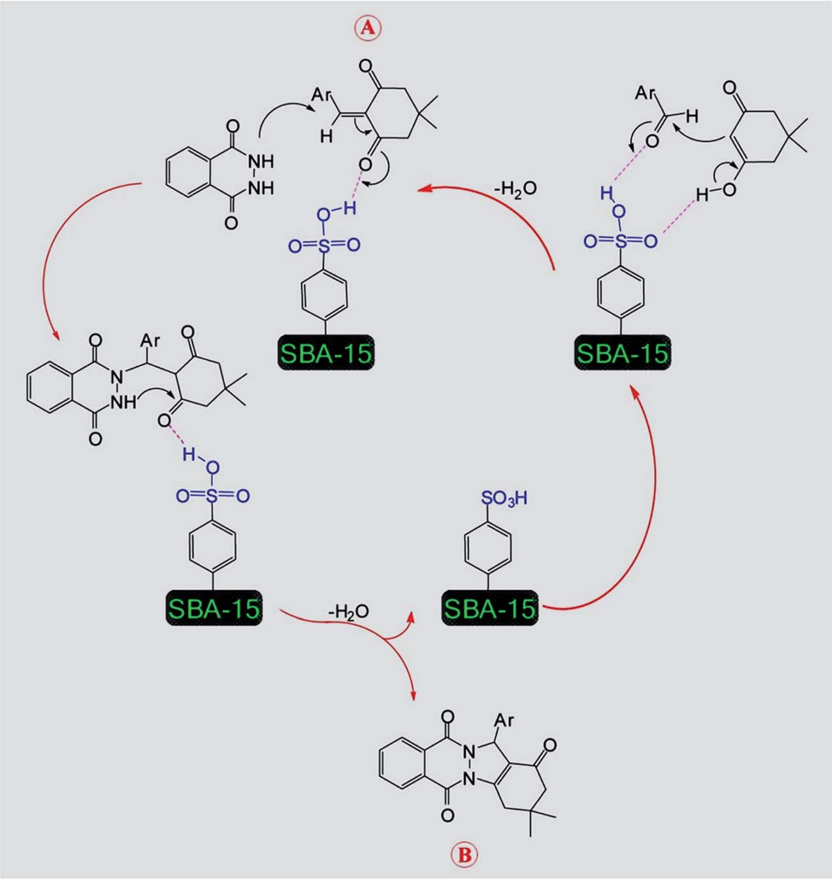

Scheme 3 Proposed mechanism for the SBA-15-Ph-SO_3H-catalyzed synthesis of indazolo[2,1-*b*]phthalazine-triones.

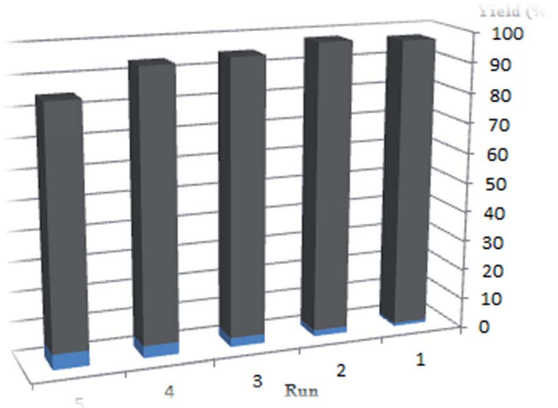

Fig. 5 The catalytic activity of SBA-15-Ph-SO_3H for five cycles of the reaction of 3-nitrobenzaldehyde, dimedone and phthalhydrazide.

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