

One Pot Synthesis of Polyhydroquinolines Catalyzed by Sulfonic Acid Functionalized SBA-15 as a New Nanoporous Acid Catalyst under Solvent Free Conditions

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ABSTRACT: Sulfonic acid functionalized SBA-15 (SBA-Pr-SO₃H) as a new nanoporous acid catalyst was used in the one-pot synthesis of polyhydroquinolines derivatives via the Hantzsch four component condensation reaction of aldehydes, β - ketoesters, dimedone and ammonium acetate under solvent free conditions with short reaction time in excellent yields. SBA-Pr-SO₃H was proved to be an efficient heterogeneous nanoporous solid acid catalyst (pore size 6 nm), which could be easily handled and removed from the reaction mixture by simple filtration, and also recovered and reused without loss of reactivity.

KEY WORDS: Nanoporous solid acid catalyst, Sulfonic acid functionalized SBA-15, Polyhydroquinolines, Solvent free conditions, Dimedone.

INTRODUCTION

1,4-Dihydropyridines possess a variety of biological activities, such as vasodilator, bronchodilator, antiatherosclerotic, antitumor, geroprotective, hepatoprotective, and antidiabetic agents [1-2].

Several efficient conditions and methods have been developed for the synthesis of 1,4-dihydropyridines such as

Hantzsch method [3], the use of microwave [4], ionic liquid [5], high temperature in refluxing solvent [6], TMSCl-NaI [7], metal triflates Yb(OTf)₃ [8], molecular iodine [9] and organocatalysts [10]. However, the use of high temperatures, expensive metal precursors and long reaction times are limiting these methods. Thus,

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the development of a simple, efficient and versatile method for the preparation of 1,4-dihydropyridine derivatives is great tendency on this research area and the entering of further improvement towards the milder reaction conditions and higher product yields is of importance in this process.

The high ordered nanoporous silica, such as MCM-41 [10], LUS-1 [11, 12] and SBA-15 [13] are unique inorganic solid supports that have very high surface area with controllable pore sizes between 2 to 30 nm. They can be employed as catalysts [14, 15], for the preconcentration of metals [16-18], and as modified carbon electrodes [19-21]. The SBA-15 is new nanoporous silica with hexagonal structure, large pore, high surface area, high thermal stability and also diffusion free due to thicker pore walls and larger pore size respectively. This can be prepared by using commercially available triblock copolymer pluronic P126 as a structure directing agent [13]. Integration of acidic functional groups (e.g., $-\text{SO}_3\text{H}$) into SBA-15 has been explored to produce promising solid acids. The sulfonic acid functionalized SBA-15 were usually synthesized through direct synthesis or post-grafting [22-23]. There have been only a few reports about the application of several types of sulfonic acid functionalized ordered mesoporous silicas as nano acid catalyst in chemical transformations [24]. For example, SBA-Pr- SO_3H has been used in the synthesis of chromenes from chromanols [25], and the *von Pechmann* reaction [26].

In this work, we would like to explore the catalytic activity of the Sulfonic acid functionalized SBA-15 (SBA-Pr- SO_3H) as a highly efficient heterogenous nanoporous acid catalyst towards the one-pot synthesis of polyhydroquinolines.

EXPERIMENTAL SECTION

Apparatus

Gc-Mass analysis was performed on a Gc-Mass model: 5973 network mass selective detector, Gc 6890 Agilent. IR spectra were recorded from KBr disk using a FT-IR Bruker Tensor 27 instrument. Melting points were measured by using the capillary tube method with an electro thermal 9200 apparatus. The ^1H -NMR (250 MHz) was run on a Bruker DPX, 250 MHz. Nitrogen adsorption and desorption isotherms were measured at -196°C using a Japan Belsorb II system after the samples were vacuum dried at 150°C overnight. Surface areas

were calculated by the Brunauer-Emmett-Teller (BET) method, and pore sizes were calculated by the Barrett-Joyner-Halenda (BJH) method. Thermogravimetry analysis (TGA) was carried out in Perkin Elmer Pyris Diamond instrument from ambient temperature to 800°C using $20^\circ\text{C}/\text{min}$ ramp rate.

Preparation of SBA-15

At First, pluronic P123 triblock copolymer surfactant ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, $M_{ac}=5800$) (4.0 g) was dissolved in 30 g of water and 120 g of 2 M HCl solution. Then, TEOS (tetraethyl orthosilicate) (8.50 g) was added to reaction mixture which was stirred for 8 h at 40°C . The resulting mixture was transferred into a teflon-lined stainless steel autoclave and kept at 100°C for 20 h without stirring. The gel composition P123: HCl: H_2O : TEOS was 0.0168:5.854: 162.681: 1 in molar ratio. After cooling down to room temperature, the product was filtered, washed with distilled water and dried overnight at 60°C in air. The as-synthesized sample was calcinated at 550°C for 6 h in air atmosphere to remove the copolymer template.

Functionalization of the SBA-15 by organic groups

Functionalization of the SBA-15 catalyst was performed according to Fig. 3. The calcinated SBA-15 (2 g) and (3-mercaptopropyl)trimethoxysilane (10 mL) in dry toluene (20 mL) were refluxed for 24 h. The product was filtered and extracted for 6h in CH_2Cl_2 using a soxhlet apparatus, then dried under vacuum. The solid product was oxidized with H_2O_2 (excess) and one drop of H_2SO_4 in methanol (20 mL) for 24 h at rt and then the mixture was filtered and washed with H_2O , and acetone. The modified SBA-15-Pr- SO_3H was dried and used as nanoporous solid acid catalyst in the following reaction.

General method for the preparation of polyhydroquinolines derivatives

The SBA-Pr- SO_3H (0.05 g) was activated in vacuum at 100°C and then after cooling to room temperature, aldehyde 1 (1.0 mmol), 5,5-dimethyl-1,3-cyclohexanedione 2 (1.0 mmol), ethyl acetoacetate 3 (1.0 mmol), ammonium acetate (1.5 mmol) were added to catalyst. Then the reaction mixture was stirred at 90°C for 5-15 min and a solid product formed. After the completion of reaction as indicated by TLC, the resulting solid product was dissolved

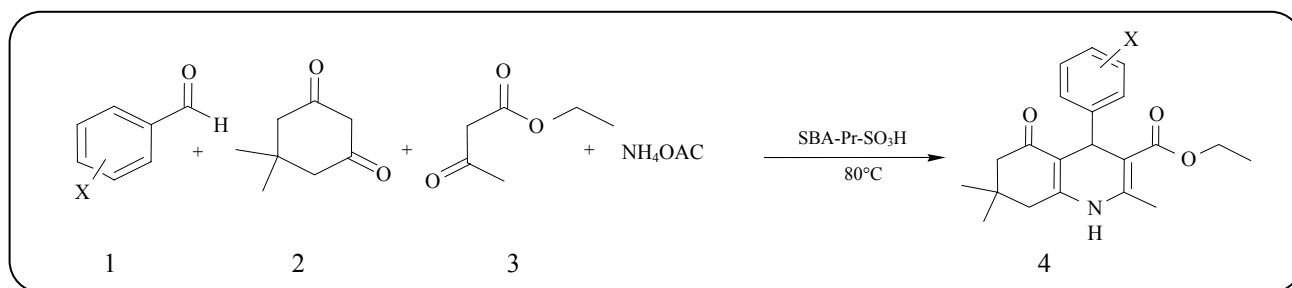


Fig. 1: Synthesis of polyhydroquinoline derivatives from aldehyde, dimedone, β -ketoesters, and ammonium acetate in the presence of SBA-Pr-SO₃H as efficient nano acid catalyst.

in hot ethanol, filtered for removing the unsolvable catalyst and then the filtrate was cooled to afford the pure product as a yellow solid. The spectroscopic and analytical data for selected compounds are presented in the following part. The catalyst was washed subsequently with acetonitrile, diluted acid solution, distilled water and then acetone, dried under vacuum and re-used for several times without loss of significant activity.

2, 7, 7-Trimethyl - 5 - oxo-4-(2,3 - dichlorophenyl)-1,4,5, 6,7, 8 - hexa-hydroquinoline - 3 - carboxylic acid ethyl ester 4b

Yellow solid; m.p: 229-234 °C; IR(KBr): 3290, 3074, 2959, 1700, 1642, 1605, 1484 cm⁻¹. ¹H NMR (250 MHz, CDCl₃): δ = 0.96 (s, 3H, CH₃), 1.07 (s, 3H, CH₃), 1.15 (t, 3H, J=7Hz, CH₂CH₃), 2.14-2.33 (m, 4H, 2*CH₂), 2.35 (s, 3H, CH₃), 4.02 (q, 3H, J=7Hz, CH₂CH₃), 5.43 (s, 1H, CH), 5.76 (s, 1H, NH), 7.05 (t, 1H, J=8Hz, ArH), 7.21 (dd, 1H, ArH), 7.31 (dd, 1H, ArH). MS: m/z (%) 407 [M⁺], 372, 262, 234.

2,7,7-Trimethyl -5- oxo-4-Isopropyl-1,4,5,6,7,8 - hexa- hydroquinoline -3-carboxylic acid ethyl ester 4e

Yellow solid; m.p: 162-164 °C; IR(KBr): 3279, 3209, 3076, 2958, 1679, 1601, 1486, 1386, 1331, 1222 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 1.00 (s, 6H, 2*CH₃), 1.08 (s, 6H, 2*CH₃), 1.23 (t, 3H, J = 7.2 Hz, CH₂H₃), 2.07-2.21 (m, 6H), 2.25 (s, 3H, CH₃), 4.01 (q, 2H, J = 7.2 Hz, CH₂CH₃), 5.86 (s, 1H, NH). MS: m/z (%) 304[M⁺], 262, 234, 218, 205, 178.

2,7,7- Trimethyl-5-oxo-4- (3,4-dimethoxyphenyl)-1,4,5,6,7,8 - hexa- hydroquinoline- 3- carboxylic acid ethyl ester 4l

Yellow solid; m.p: 207-209 °C; IR (KBr): 3278, 3078, 2936, 1965, 1603, 1489, 1308, 1217 cm⁻¹. ¹HNMR (250

MHz, CDCl₃): δ = 0.95 (s, 3H, CH₃), 1.08 (s, 3H, CH₃), 1.21 (t, 3H, J = 7Hz, CH₂CH₃), 2.2-2.32 (m, 4H, 2*CH₂), 2.38 (s, 3H, CH₃), 3.80 (s, 3H, OCH₃), 3.83 (s, 3H, OCH₃), 4.08 (q, 2H, J= 7 Hz, CH₂CH₃), 5.01 (s, 1H, CH), 5.63 (s, 1H, NH), 6.68-6.76 (m, 2H, ArH), 6.92 (d, 1H, ArH). Ms: m/z (%) 399 [M⁺] 370, 354, 326, 262, 234.

2,7,7-Trimethyl-5-oxo-4-(3-methoxyphenyl)-1,4,5, 6, 7, 8 - hexa- hydroquinoline-3-carboxylic acid ethyl ester 4m

Yellow solid, m.p: 208-211. IR (KBr): 3302, 3076, 2959, 1696, 1645, 1610, 1483 cm⁻¹. ¹HNMR (250 MHz, CDCl₃): δ = 0.95 (s, 3H, CH₃), 1.07 (s, 3H, CH₃), 1.2 (t, 3H, J = 7 Hz, CH₂CH₃), 2.12-2.28 (m, 4H, 2*CH₂), 2.39 (s, 3H, CH₃), 3.75 (s, 3H, OCH₃), 4.08 (q, 2H, J = 7 Hz, CH₂CH₃), 5.04 (s, 1H, CH), 5.93 (s, 1H, NH), 6.62-7.2 (m, 5H, Ar H). MS: m/z (%) 369 [M⁺], 340, 324, 296, 262, 234.

RESULTS AND DISCUSSION

The classical method for the preparation of polyhydroquinolines derivatives involves the reaction of aldehydes with ethyl acetoacetate, and ammonia in acetic acid or in refluxing alcohol. However, this method suffers from several disadvantages such as long reaction times, excess of organic solvent, lower product yields and refluxing conditions. Therefore, after using MCM-41 in this synthesis by Nagarapu [27], and in continuation of our studies on the application of new acid catalysts in organic synthesis [28], we had the opportunity to explore the catalytic activity of nanoporous catalyst of SBA-Pr-SO₃H towards the synthesis of 1,4-dihydropyridines from aldehyde, dimedone, β -ketoesters, and ammonium acetate under solvent free conditions as shown in Fig. 1. The reaction has efficiently been carried out in excellent yields with short reaction time. The results were summarized in Table 1.

Table 1: The SBA-Pr-SO₃H catalyzed the synthesis of polyhydroquinoline derivatives.

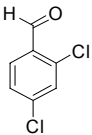
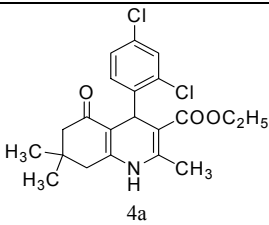
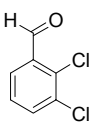
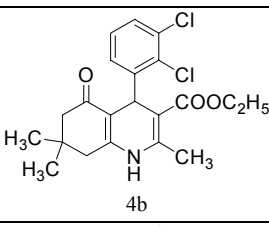
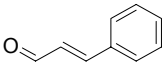
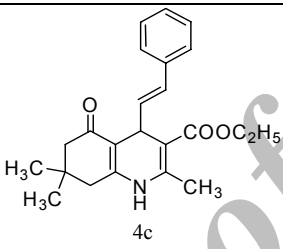
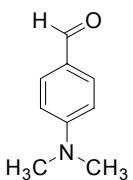
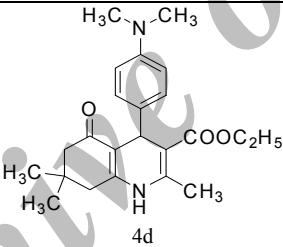
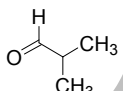
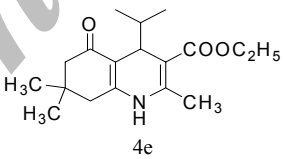
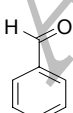
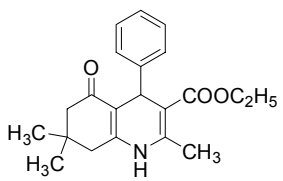
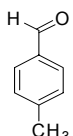
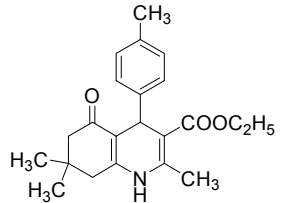
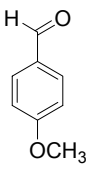
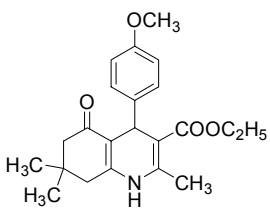
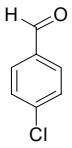
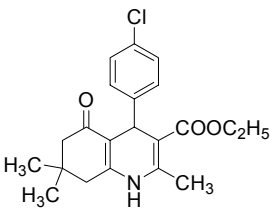
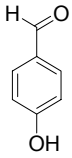
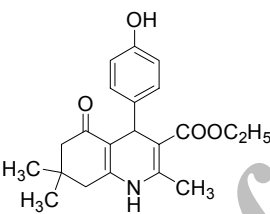
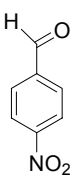
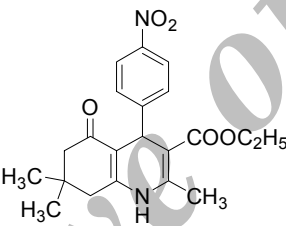
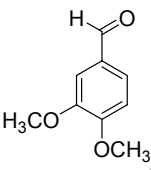
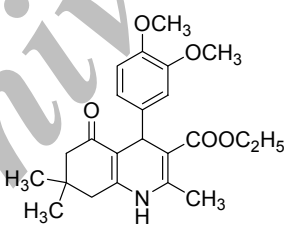
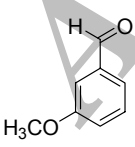
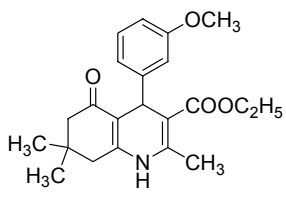
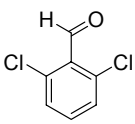
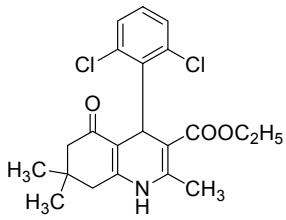
Entry	Aldehyde	Product	Time/min	Yield %	mp/°C	Ref.
1		 4a	13	80	241-244	241-244 [29b]
2		 4b	13	80	229-234	--
3		 4c	12	90	204-206	204-206 [30]
4		 4d	12	85	231-233	229-231 [29b]
5		 4e	18	80	162-166	-
6			10	85	227-230	227-229 [31]
7			10	90	260-262	260-262 [31]

Table 1: (continued)

8			12	90	264-266	260-261 [32]
9			12	85	242-244	245-246 [29a]
10			12	90	239-240	238-240 [32]
11			10	85	242-244	242-244 [30]
12			10	90	207-209	-
13			10	90	208-211	--
14			14	75	241-244	241-244 [29b]

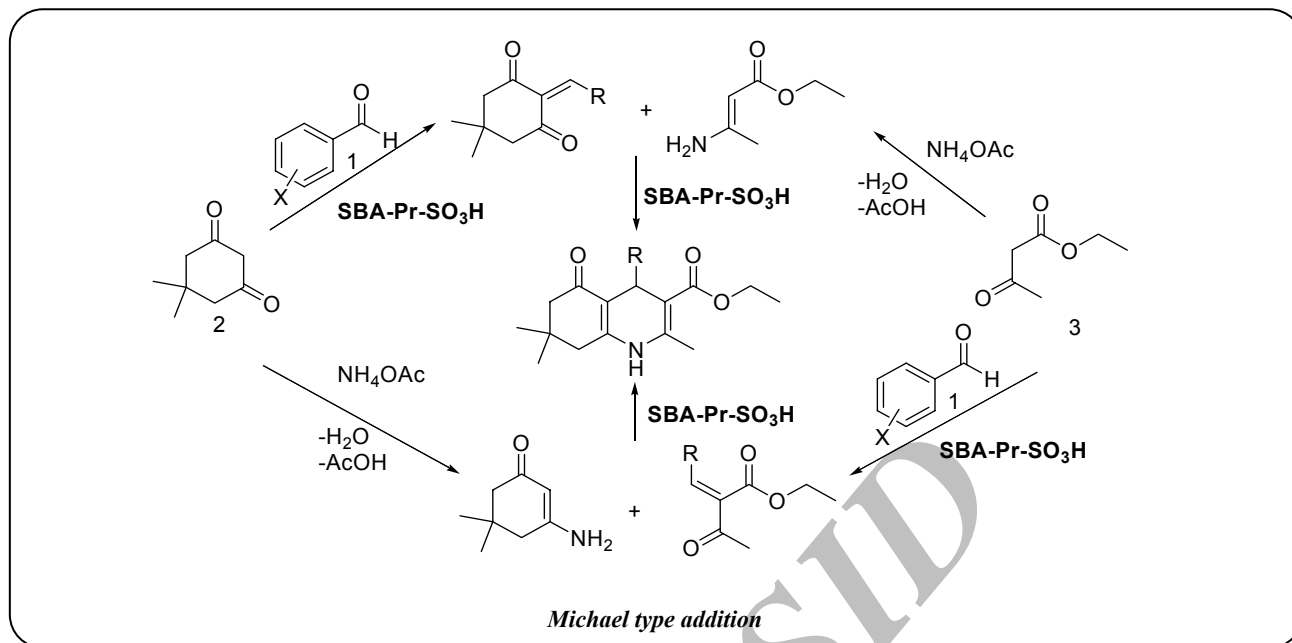
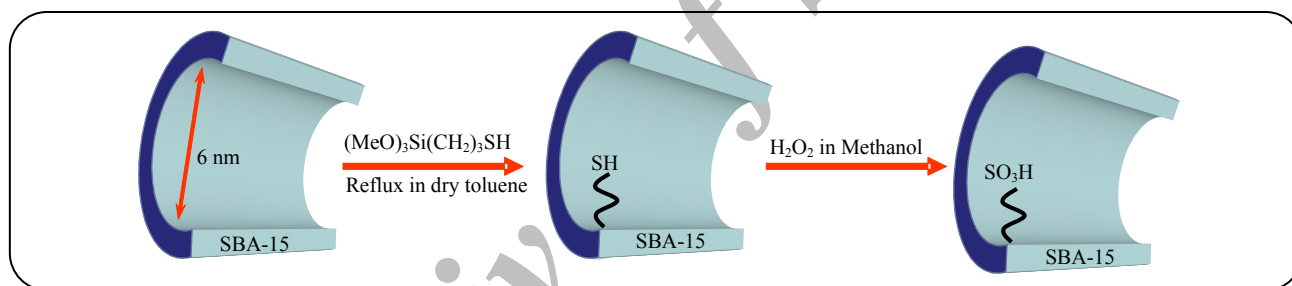


Fig. 2: The proposed mechanism.

Fig. 3: Schematic illustration for the preparation of SBA-Pr-SO₃H.

The proposed mechanism was shown in Fig. 2. The polyhydroquinoline derivatives could be synthesized by two methods. The SBA-Pr-SO₃H catalyses subsequently the *Knoevenagel* type coupling of aldehydes with active methylene compounds and then the *Michael* type addition of intermediates together to provide the products [29a].

Knoevenagel condensation

Preparation and characterization of catalyst

Pure Nanoporous compound SBA-15 was synthesized according to the well-established method designed by Zhao & coworkers [13] with triblock poly(ethylene oxide)-b-poly(propylene oxide)-bpoly(ethylene oxide) copolymer (Pluronic, EO₂₀PO₇₀EO₂₀, P123) as the template. A schematic illustration for the preparation of SBA-Pr-SO₃H was shown in Fig. 3. First, the calcined SBA-15 silica was functionalized with (3-mercaptopropyl)

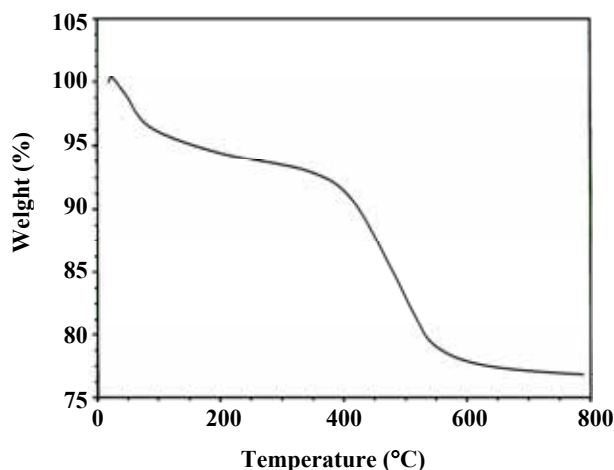
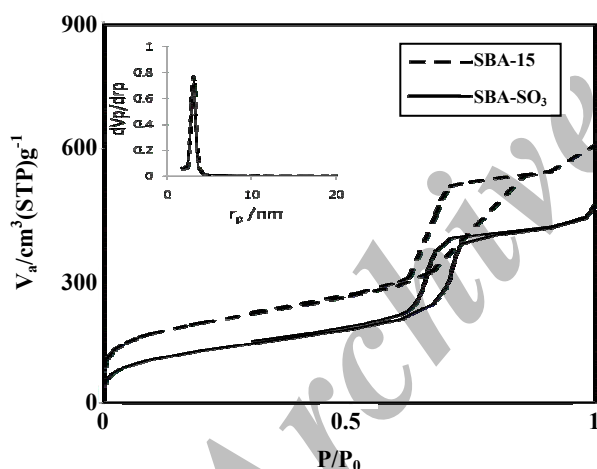
trimethoxysilane (MPTS) and then, the thiol groups were oxidized to sulfonic acid by hydrogen peroxide.

The TGA analysis of SBA-Pr-SO₃H (Fig. 4) confirmed the amount of organic groups on SBA-15. The weight reduction of SBA-Pr-SO₃H in the temperature range between 200-600°C indicated that the amount of organic group was 1.2 mmol/g.

The nitrogen adsorption-desorption isotherms for SBA-15 and SBA-Pr-SO₃H are shown in Fig. 5. Both materials show type-IV adsorption behavior with the hysteresis loops appearing at relatively high pressure, suggesting that the prepared samples have regular mesoporous framework structures. Their texture properties are given in Table 2. The surface area, average pore diameter calculated by the BET method and pore volume of SBA-Pr-SO₃H are 440 m²g⁻¹, 6.0 nm and 0.660 cm³ g⁻¹, respectively, which are smaller than those

Table 2. Porosimetry values for SBA-15 and functionalized SBA-15.

	Surface area (cm ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore diameter (nm)
SBA-15	649	0.806	6.2
SBA-SO ₃ H	440	0.660	6.0

**Fig. 4: Thermogravimetric analysis (TGA) of SBA-Pr-SO₃H.****Fig. 5: N₂ adsorption-desorption isotherms and pore size distribution (inset) for SBA-15 (---) and SBA-Pr-SO₃H (—).**

of SBA-15 due to the immobilization of sulfonosilane groups into the pores.

CONCLUSIONS

In conclusion, an efficient synthesis of polyhydroquinolines derivatives has been achieved via a one-pot four component reaction of aromatic aldehydes, dimedone, β -ketoesters, and ammonium acetate under

solvent free conditions using the reusable and environmentally benign sulfonic acid functionalized nanoporous SBA-15 as solid acid catalyst. The reasonable reaction time, very good to excellent yields, simple workup procedure, and environmentally friendly conditions are main merits of this method. Therefore SBA-Pr-SO₃H can be used as an efficient heterogenous catalyst such as other catalysts in organic syntheses [33].

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