

# Sulfonic acid functionalized mesoporous SBA-15 for selective synthesis of 4-phenyl-1,3-dioxane

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## Abstract

Mesoporous SBA-15 silica has been functionalized with propylsulfonic acid groups post-synthetically using 3-mercaptopropyltrimethoxysilane as sulfur source. The materials before and after functionalization have been characterized by BET surface area and pore size distribution by BJH method, powder X-ray diffraction and temperature programmed desorption (TPD) of  $\text{NH}_3$ . The resultant mesoporous material (solid acid catalyst) exhibited hexagonal mesoscopic ordering, which possess  $1.3 \text{ meq H}^+ \text{ g}^{-1} \text{ SiO}_2$  exchange capacity,  $96 \text{ \AA}$  mesopore size diameter, and  $660 \text{ m}^2 \text{ g}^{-1}$  surface area. Sulfonic acid groups anchored to SBA-15 silica pore surfaces are thermally stable up to  $653 \text{ K}$ , hydrothermally robust in boiling water and resistant to leaching in organic and aqueous solvents under mild conditions. XRD results indicate that there is no change in the structure after anchoring SBA-15 with  $\text{SO}_3\text{H}$  group. SBA-15- $\text{SO}_3\text{H}$  catalyst has been found to be highly active and selective for the Prins condensation of styrene with formaldehyde. Both the conversion of styrene and the selectivity to 4-phenyl-1,3-dioxane are nearly 100%. Presence of more number of acid sites in SBA-15- $\text{SO}_3\text{H}$  catalyst helps in achieving high yields. Furthermore, the conversion and the selectivity to 4-phenyl-1,3-dioxane are found to be consistent in four repeated cycles. © 2006 Elsevier B.V. All rights reserved.

**Keywords:** SBA-15; Prins condensation; Styrene; 4-Phenyl-1,3-dioxane; SBA-15- $\text{SO}_3\text{H}$

## 1. Introduction

Dioxane and its derivatives are typically synthesized by the Prins condensation of olefins with aldehydes under homogeneous catalysis conditions in presence of either strong mineral acids (e.g.,  $\text{H}_2\text{SO}_4$ ) or Lewis acids [1–4]. These acids are highly corrosive, generate a large amount of toxic waste and involve tedious separation procedures. In recent times, solid acid catalysts such as clays [5,6], zeolites [7,8] and mesoporous materials [9,10] have received a considerable attention in organic synthesis because of their environmental compatibility, reusability, high selectivity, operational simplicity, non-corrosiveness, low cost and

ease of isolation of the products. In particular, sulfonic acid functionalized mesoporous solid acid catalysts are emerging as versatile catalysts for various condensation reactions [11,12].

The concept of using sulfonic acids as solid acid catalysts may not be completely new, since the commercial sulfonated resins such as Amberlyst –15 and Nafion–H are widely available for several years [13]. However, the practical utility of these catalysts has been hampered due to low surface area (i.e.,  $<1 \text{ m}^2 \text{ g}^{-1}$ ). Subsequently, high surface area sulfonated mesoporous MCM-41 type solid acid catalysts have been developed [14,15], but faced serious drawback of low hydrothermal stability [16–18]. In 1998, high surface area, large pore size, greater pore wall thickness, hydrothermally robust and hexagonally ordered mesoporous SBA-15 silica was synthesized [19]. Since then, SBA-15 was modified to suit for different catalytic applications [20]. Accordingly, SBA-15 was modified as a solid acid

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catalyst with sulfonic acid functionalization (SBA-15-SO<sub>3</sub>H) [21]. However, SBA-15-SO<sub>3</sub>H solid acid catalyst has not been reported so far for the Prins condensation reactions. In the present investigation, 4-phenyl-1,3-dioxane was synthesized selectively by the Prins condensation of styrene with formaldehyde using highly active SBA-15-SO<sub>3</sub>H solid acid catalyst.

## 2. Experimental

### 2.1. Preparation of SBA-15-SO<sub>3</sub>H catalyst

A solution of EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>: 2 M HCl:TEOS:H<sub>2</sub>O = 2:60:4.25:15 (mass ratio) was prepared, stirred for 12 h at 313 K and then heated at 373 K for 12 h, subsequently filtered and calcined at 773 K for 8 h to get mesoporous silica (SBA-15). A mixture of 3.0 g of SBA-15 (evacuated at 423 K) and 5.301 g of 3-mercaptopropyltrimethoxysilane (MPTS) in dry toluene was refluxed for 6 h and the solid (-SH) was filtered, washed with dry toluene and dried in air. The -SH groups were converted to -SO<sub>3</sub>H groups by mild oxidation with H<sub>2</sub>O<sub>2</sub> by continuous stirring at 333 K for 24 h. The solid was filtered off, washed with water and ethanol, respectively, and acidified under refluxing condition with 0.1 M H<sub>2</sub>SO<sub>4</sub>, followed by thorough washing with water, filtered off and dried at 333 K for 12 h.

### 2.2. Characterization techniques

Low angle X-ray diffractograms were recorded on a Philips PW 1840 powder diffractometer using Ni filtered Cu K $\alpha$  radiation in the 2 $\theta$  range of 0.5–6°. Pore size distribution was obtained from the nitrogen adsorption-desorption isotherms of calcined SBA-15 and SBA-15-SO<sub>3</sub>H. The N<sub>2</sub> adsorption-desorption measurements were performed at 77 K using automated gas sorption system (M/S. Quantachrome, USA) utilizing Brunner-Emmett-Teller (BET) calculation for surface area and Barrett-Joyner-Halanda (BJH) method for pore size distribution. Temperature programmed desorption (TPD) of NH<sub>3</sub> experiments were carried out using a procedure described elsewhere [22]. Sulfur loading has been estimated using elemental analyzer (Model: VARIO El, Make: Elementar, Germany). In a typical experiment 1 mg of sample was taken in to a tin boat. By using auto sampler, the sample was introduced in to the combustion tube, which was maintained at 1423 K. Combustion took place in presence of O<sub>2</sub> and respective oxides were formed and passed through reduction tube. The gases formed were pumped to respective columns with He as carrier gas and were detected by thermal conductivity detector. Sulfonic acid was used as internal standard.

### 2.3. Activity studies

The catalytic activity of SBA-15-SO<sub>3</sub>H catalyst for the condensation of styrene (1.041 g, 10 mmol) with 38% aque-

ous solution of formaldehyde (1.58 g, 20 mmol) over 100 mg catalyst was carried in a 25 ml round bottom flask with 5 ml of solvent under refluxing temperature for 35 h. The reaction was also conducted at 413 K in autoclave under autogenous pressure for 4 h. The identification and quantification of the product have been done using GC-MS (Shimadzu, QP5050) equipped with DB5-MS capillary column (0.32 m.m. i.d. and 30 m length). The column temperature was increased starting from 333 K to 523 K at 8 K/min and was kept under isothermal conditions for 4 min at 523 K. The conversion of styrene is calculated as the ratio between the number of moles of styrene converted to the total number of moles of styrene in the reaction mixture and multiplied by 100. The % selectivity of 4-phenyl-1,3-dioxane is calculated as follows:

$$= \frac{\text{No. of moles of 4-phenyl-1,3-dioxane produced}}{\text{No. of moles of styrene converted}} \times 100.$$

## 3. Results and discussion

SBA-15 has been synthesized in accordance with the procedures reported in the previous work [9], using triblock copolymer (P123) as structure directing agent and tetraethylorthosilicate as silica source under acidic conditions. The -SH functionalization has been made post-synthetically using 3-mercaptopropyltrimethoxysilane as sulfur precursor and its oxidation to -SO<sub>3</sub>H has been done according to the literature report [10]. Sulfur loadings are found to be about 1.41 and 1.28 meq g<sup>-1</sup> in the functionalized form and in its oxidized form, respectively. The structural intactness and hydrothermal stability have been tested after -SH functionalization and its oxidation. No change in the sulfur content has been observed after the catalyst has been refluxed in water for 3 h.

SBA-15 material thus prepared had a BET surface area of 669 m<sup>2</sup> g<sup>-1</sup> with pore volume of 1.61 cm<sup>3</sup> g<sup>-1</sup>, pore size 96.4 Å and pore wall thickness 24 Å (Fig. 1) The small-angle XRD patterns (Fig. 2) for SBA-15 and SBA-15-SO<sub>3</sub>H showed well-resolved peaks, which are indexable as (100), (110), (200) and (210) reflections with p6 mm hexagonal symmetry. The intense (100) peak reflects a *d* spacing of 104 Å corresponding to large unit-cell parameter (*a*<sub>0</sub> = 120 Å). Reproducibility of the physical characteristics after stirring the SBA-15 in boiling water for 24 h is an indication of its hydrothermal stability. The lattice parameters (*a*<sub>0</sub>) of SBA-15 and SBA-15-SO<sub>3</sub>H are shown in Table 1. There is not much change between the lattice parameters for large unit cell (*d*<sub>100</sub>) of SBA-15 and that of SBA-15-SO<sub>3</sub>H. Fig. 3 represents the temperature programmed desorption (TPD) of NH<sub>3</sub> patterns. Curve (a) represents the TPD pattern of SBA-15. Small intense but broad NH<sub>3</sub> desorption signal can be seen in this pattern. Curve (b) is the TPD pattern of SBA-15-SO<sub>3</sub>H before subjecting to the NH<sub>3</sub> adsorption. Even in the absence of NH<sub>3</sub> adsorption, SBA-15-SO<sub>3</sub>H shows desorption pattern cen-

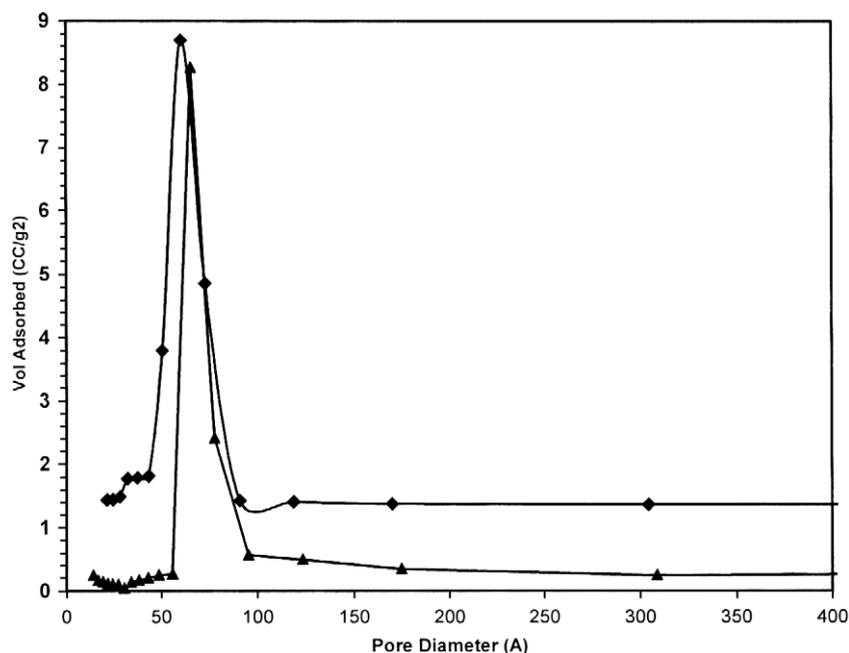


Fig. 1. The pore size distribution curve of calcined (◆) SBA-15 (▲) SBA-15-SO<sub>3</sub>H N<sub>2</sub> adsorption measurements were performed at 77 K using quantachrome autosorb automated gas sorption system utilizing Barrett–Joyner–Halanda (BJH) calculation for pore volume and pore size distributions.

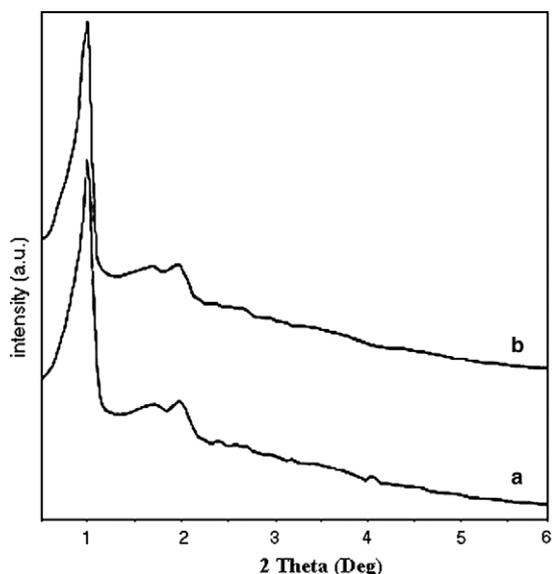


Fig. 2. X-ray diffractograms of (a) SBA-15 and (b) SBA-15-SO<sub>3</sub>H.

Table 1  
Lattice parameters of (a) SBA-15 and SBA-15-SO<sub>3</sub>H

Catalyst	<i>hkl</i>	<i>d</i> (Å)	<sup>a</sup> <i>a</i> <sub>0</sub> (Å)
SBA-15	100	104.5	120.7
	110	54.1	
	200	46.7	
SBA-15-SO <sub>3</sub> H	100	102.7	118.6
	110	52.1	
	200	44.2	

<sup>a</sup> Large unit cell parameter (*a*<sub>0</sub>) = 2*d*(100)/(3)<sup>1/2</sup>.

tered at a  $T_{\max}$  of  $\sim 873$  K and another small intense signal centered at a  $T_{\max}$  of 653 K. These signals are probably due to the decomposition/desorption of SO<sub>3</sub>H groups. This is an indication that SBA-15-SO<sub>3</sub>H is thermally stable up to 653 K. Curve (c) is the TPD of NH<sub>3</sub> pattern of SBA-15-SO<sub>3</sub>H. The total number of acid sites as determined by temperature programmed desorption of ammonia is found to be much higher in the case of SBA-15-SO<sub>3</sub>H catalyst (1251  $\mu\text{mol g cat}^{-1}$  (corrected for the decomposition of SO<sub>3</sub>H group)) when compared to bare SBA-15 (134  $\mu\text{mol g cat}^{-1}$ ).

The results of Prins condensation of styrene with formaldehyde over different catalysts including H<sub>2</sub>SO<sub>4</sub> are summarized in Table 2 (S. Nos. 1–6). In the absence of a catalyst, styrene conversion is 10%. Even at this low conversion, the selectivity to 4-phenyl-1,3-dioxane is only 50%. It is known that H<sub>2</sub>SO<sub>4</sub> is a conventional Prins condensation catalyst however, H<sub>2</sub>SO<sub>4</sub> as a catalyst exhibited 100% styrene conversion but could not maintain 100% selectivity towards 4-phenyl-1,3-dioxane as expected. The conversion of styrene over H-ZSM-5 is 66% and the selectivity towards 4-phenyl-1,3-dioxane is only 17%. The conversion of styrene over bare SBA-15 is 9%, which is comparable with the results obtained in the absence of a catalyst, but maintained 100% selectivity towards 4-phenyl-1,3-dioxane. The low activity of bare SBA-15 is speculated to the lack of required number and strength of acidic sites and the high selectivity towards 4-phenyl-1,3-dioxane, may be assigned to its mesoporous network. SBA-15-SO<sub>3</sub>H solid acid catalyst exhibited an excellent performance in the condensation of styrene with formaldehyde for the synthesis of 4-phenyl-1,3-dioxane with 100% yield. We believe

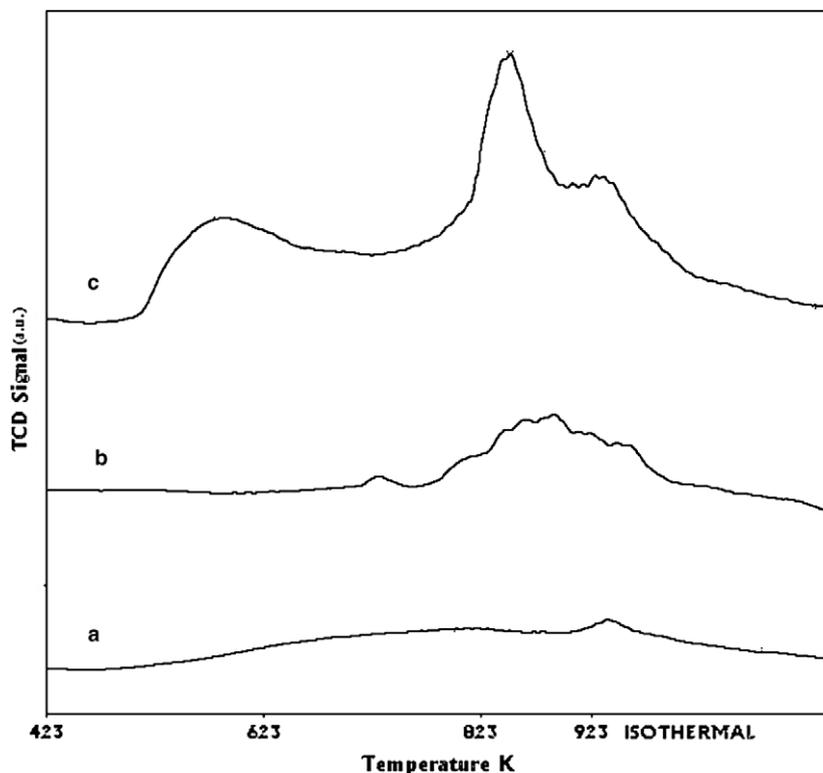


Fig. 3. Temperature programmed desorption (TPD) of  $\text{NH}_3$  of: (a) SBA-15 after  $\text{NH}_3$  adsorption; (b) SBA-15- $\text{SO}_3\text{H}$  without  $\text{NH}_3$  adsorption and (c) SBA-15- $\text{SO}_3\text{H}$  (after  $\text{NH}_3$  adsorption).

Table 2  
Synthesis of 4-phenyl-1,3-dioxane over different catalysts using different solvents

S. No.	Catalyst	Solvent	Conversion (mole%)		
			Styrene	4-Phenyl-1,3-dioxane	Others
1	Without catalyst	Dichloromethane	10	50	50
2	$\text{H}_2\text{SO}_4$	Dichloromethane	~100	84	16
3	H-ZSM-5	Dichloromethane	66	17	83
4	SBA-15	Dichloromethane	9	~100	0
5	SBA-15- $\text{SO}_3\text{H}$	Dichloromethane	~100	~100	0
6	SBA-15- $\text{SO}_3\text{H}^a$	Dichloromethane	~100	~100	0
7	SBA-15- $\text{SO}_3\text{H}$	Without solvent	74	~100	0
8	SBA-15- $\text{SO}_3\text{H}$	Water	69	52	48
9	SBA-15- $\text{SO}_3\text{H}$	1,2-dichloroethane	10	~100	0
10	SBA-15- $\text{SO}_3\text{H}$	Toluene	80	~100	0
11	SBA-15- $\text{SO}_3\text{H}$	Carbon tetrachloride	64	97	3
12	Recycled – 1	Dichloromethane	99	~100	0
13	Recycled – 2	Dichloromethane	99	~100	0
14	Recycled – 3	Dichloromethane	99	~100	0

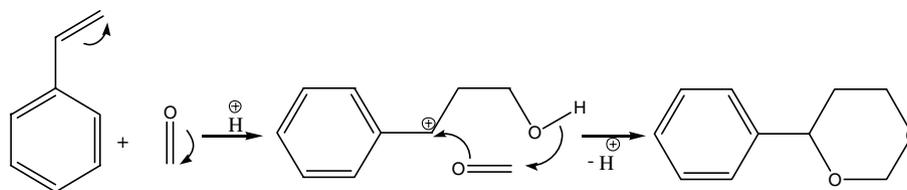
Catalyst = 0.1 g, styrene = 1.041 g, formaldehyde = 1.578 g, styrene:formaldehyde = 1:2 (molar ratio), solvent = 5 ml, reaction time = 35 h.

<sup>a</sup> 4 h (under autogenous pressure).

that the accessibility of large number of the active sites for the reactants will be more in SBA-15- $\text{SO}_3\text{H}$  solid acid catalyst due to regular and well ordered hexagonal array of mesopores present in the SBA-15 support providing nano-sized micro-reactors for the reaction. The reaction conducted in an autoclave at a temperature of 413 K under autogenous pressure over SBA-15- $\text{SO}_3\text{H}$  catalyst using dichloromethane as solvent showed  $\approx 100\%$  conversion

and 100% selectivity towards 4-phenyl-1,3-dioxane with in 4 h.

The results reveal (Table 2, S. Nos. 5–11) that the solvents have profound influence on catalytic activity as well as product distribution over SBA-15- $\text{SO}_3\text{H}$  solid acid catalyst. Dichloromethane solvent plays a unique role in obtaining 100% conversion of styrene and 100% selectivity towards 4-phenyl-1,3-dioxane in comparison with other



Scheme 1. Prins condensation of styrene with formaldehyde.

solvents used in the present publication. High activity (conversion = 74% and selectivity = 100%) has also been observed even in the absence of a solvent. It is thought that water content in the 38% formaldehyde aqueous solution might have compensated for the solvent. Our results suggest that an organic solvent may not be required for high activity if aqueous solution of formaldehyde is used instead of paraformaldehyde. Further more, aqueous solution of formaldehyde is a very attractive substrate from industrial point of view [23]. Synthesis of 4-phenyl-1,3-dioxane over SBA-15-SO<sub>3</sub>H without using organic solvents is ultimately cost-effective and eco-friendly. Unfortunately, we observed that organic solvents are needed for catalyst separation in the solvent free catalytic system. When water is used as solvent, conversion of styrene is decreased to 69% and also the selectivity towards 4-phenyl-1,3-dioxane is dropped to 52%. This may be related to poor kinetic transportation in water medium beside the solvent effect. The conversion of styrene over SBA-15-SO<sub>3</sub>H catalyst with 1,2-dichloroethane and toluene are 10% and 80% respectively, with 100% selectivity towards 4-phenyl-1,3-dioxane. In the case of carbon tetrachloride solvent the styrene conversion is 64% with 97% 4-phenyl-1,3-dioxane selectivity has been observed. The activity trend of the catalyst in different solvent medium (Table 2, S. Nos. 5–11) is as follows: 1, 2-dichloroethane < water < carbon tetrachloride < toluene < dichloromethane.

The effect of solvents on the present catalyst has not yet been fully understood.

Prins condensation proceeds with the protonation of formaldehyde on a Bronsted acid site, which further reacts with styrene to form a secondary carbocation. The secondary carbocation reacts with formaldehyde by proton abstraction and forms 4-phenyl-1,3-dioxane (scheme 1). The secondary carbocation can also be transformed into several unwanted by-products. There is a lot of possibility for a series of secondary processes such as oligomerization, aromatization and cracking that complicate the reaction network. However, no such problem was observed on SBA-15-SO<sub>3</sub>H solid acid catalyst.

Recently, the syntheses of 4-phenyl-1,3-dioxane with 91% yield over indium bromide Lewis acid catalyst using ionic liquids as a solvent has been reported [24]. This is the maximum yield reported so far under heterogeneous conditions. Similar high activity has also been reported over molybdovanadophosphoric heteropolyacid homogeneous catalyst with 99.9% styrene conversion and 98.7% 4-phenyl-1,3-dioxane selectivity [25]. Although, this cata-

lyst is highly active, it presents serious drawbacks as a homogeneous catalyst. SBA-15-SO<sub>3</sub>H solid acid catalyst seems to be superior to the reported heterogeneous catalysts [24] for the Prins condensation of styrene with formaldehyde for the selective synthesis of 4-phenyl-1,3-dioxane and also on par with the highly selective homogeneous catalyst [25].

SBA-15-SO<sub>3</sub>H solid acid catalyst was tested for its reusability (Table 2, S. Nos. 5, 12–14). No appreciable loss in activity from first cycle to subsequent cycles was noticed.

The results on SBA-15-SO<sub>3</sub>H solid acid catalyst with dichloromethane solvent seem to be much better for the synthesis of 4-phenyl-1,3-dioxane, compared to the conversion and selectivity reported so far. We believe that such high conversion and selectivity to nearly 100% is reported for the first time on SBA-15-SO<sub>3</sub>H in the presence of dichloromethane solvent medium. Furthermore, SBA-15-SO<sub>3</sub>H solid acid catalyst is inexpensive, non-toxic and reusable which makes the process convenient, economical and environmentally benign.

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