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**(Research Article)**

# Sulphonation of Aromatics using Silica Sulphuric acid/ $NaHSO_4$ as a Novel Heterogeneous System at Ambient Temperature

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**ABSTRACT**
*Using Silca sulphuric acid/ $NaHSO_4$ and wet $SiO_2$ as novel heterogeneous catalyst, the aromatic sulphonic acids were synthesized in good yields. The reaction was carried out at room temperature and involved simple workup. The possibility of reuse of the catalyst was also investigated. The results indicated that the aromatic sulphonation procedure could be carried out under mild conditions and the recycling of the catalyst is possible thus making the whole process more eco-friendly.*

**Key Words:** Silca sulphuric acid/ $NaHSO_4$, Wet $SiO_2$, Heterogeneous catalyst, Aromatic Sulphonic acids

## INTRODUCTION

Aromatic sulphonic acids find a variety of industrial applications. Alkyl naphthalene sulphonates (ANS) are used as nondetergent wetting agents. The agriculture industry uses ANS in wettable formulations, whereas the textile industry uses ANS for bleaching and dyeing operations. Sulphonic acid derivatives are used industrially on a large scale in the production of detergents. The most widely used synthetic detergents are sodium salts of alkylbenzenesulphonic acids. Aromatic sulphonic acids are also used as acid catalysts in Organic reactions viz. p-toluene sulphonic acid in acetalization of aldehyde[1], esterification of carboxylic acids[2]. Aromatic sulphonic acids and salts thereof are immunocorrectors[3] , viral inhibitors[4]. Aromatic sulphonic acids are synthesized via electrophilic aromatic substitution reaction which utilizes excess of concentrated Sulphuric acid[5, 6, 7], resulting in the generation of a huge amount of spent acid. This acidic effluent, if untreated can cause potential hazards to environment. The rising environmental awareness and regulations have necessitated the modification of the existing processes to more eco-friendly processes. Thus Heterogeneous acid catalysts are gaining importance in the development of greener technologies. Use of the heterogeneous catalysis offers easier separation, possibility of recycling of the catalyst and a reduction in the waste generation. Silica sulphuric acid is an excellent proton source[8,] easy to prepare and hence utilized in many reactions as a replacement of sulphuric acid[8, 9, 10]. Stability, [8] low toxicity, ease of handling, non corrosivity[8, 11] ease of separation and reusability of Silica sulphuric acid catalyst makes it promising for academic and industrial settings[11]. $NaHSO_4$ adsorbed on silica gel is an excellent proton source and has a higher catalytic activity than many other heterogenous acid catalysts which are sensitive to moisture and also very expensive[12].So far it has been used for synthesis of homoallylic amines[13] , cleavage of phenyl esters[14]. Nitration of aromatic nucleus[9] and development of trityl ethers[15]. Microwave assisted aromatic sulphonation with $NaHSO_4$ and silica sulphuric acid has been reported. However the use of catalyst along with $NaHSO_4$ and wet $SiO_2$ for the aromatic sulphonation is not reported so far to the best of our knowledge. We wish to report an efficient method which can be carried out at ambient temperature for

synthesis of arylsulphonic acid with Silica sulphuric acid / $NaHSO_4$ and wet $SiO_2$ for sulphonation of aromatic compounds with reusability of catalyst (Fig.1). The plausible mechanism for in-situ generation of sulphonating agent from immobilized silica sulphuric acid is given in Fig. 2.
The objective of the work was to develop an improved procedure for the aromatic sulphonation reactions. We started with sulphonation of toluene and then extended the same reaction to study the sulphonation of other substituted aromatic substrates as well as polyaromatic substrates. (Table 1)

## MATERIALS AND METHODS

### Chemistry

Purity of the starting materials used in the reaction was confirmed by melting point, boiling point. The purity and structure of compounds synthesized were confirmed by melting point, boiling point, Infrared (IR) Spectroscopy and Nuclear Magnetic Resonance (NMR) Spectroscopy. The melting point of the compounds reported were uncorrected and were recorded by open capillary method on THERMONIK-Campbell Melting Point apparatus and they were in good agreement with the literature reported values. The following instruments were used: Schimadzu Fourier-transform–infrared (FT-IR) 8400S. IR spectra were recorded using KBr pellet, and 1H NMR spectra were measured at 300MHz in DMSO solution with tetramethylsilane (TMS) as internal standard. Evaporation of solvent was performed in a rotary evaporator under reduced pressure. All the solvents used in reactions were commercial grade and used as such without purification. All the chemicals were obtained from S.D. Fine Chemicals Pvt. Ltd., Mumbai and used without further purification.

### Experimental

*Preparation of silica sulphuric acid*[16]

100 ml round bottom flask was charged with silica gel (3 g). Chlorosulfonic acid (1.15 g) was added dropwise over a period of 30 min at room temperature. HCl gas immediately evolved from the reaction vessel. After complete addition, the reaction mixture was stirred (or shaken) for 30 min. A white solid of silica sulfuric acid (3.6g, 94.73%) was obtained.

*Typical Procedure for preparation of 4-toluene sulphonic acid*

A suspension of Toluene (0.1 g, 1 mmol), Silica Sulphuric acid (0.38g, 1 mmol), $NaHSO_4.H_2O$ (0.552 g, 4 mmol) and Wet $SiO_2$ (50% w/w, 0.2g) in $CH_2Cl_2$ (15 ml) was stirred on a magnetic stirrer at room temperature for 4 hrs. After the completion of reaction (as monitored by TLC) mixture was filtered. The residue was washed with $CH_2Cl_2$ (2 × 10 ml); solvent was then removed under reduced pressure. The residue left behind was washed with n-hexane (2 × 10 ml) and dried in an air to produce white solid (0.14g,75 % yield). The product was purified by recrystallization. M. P.: 99-103.

IR (KBr): $cm^{-1}$ 3402, 1650, 1209, 1095

$^1$H NMR: (300 MHz, DMSO-$D_6$): δ 7.5(d, 2H, aromatic), 7.15(d, 2H, aromatic) and 2.25(s, 3H, $CH_3$)

*Reusability of the catalyst*

The catalyst, Silica Sulphuric acid obtained by filtration of the reaction mixture was washed with two 10 ml portion each of ethyl acetate [8] and dried under vacuum to constant weight at room temperature. It was then reused in five consecutive runs for the synthesis of 4-toluenesulphonic acid by the procedure described above. Table-2 shows the yields obtained by reuse of the catalyst in each of the five runs. As evident from Table-2 the decrease in the yield of the reaction is only marginal leading to the conclusion that the catalyst can be reused for atleast 5 runs.

## RESULTS AND DISCUSSION

Sulphonation of aromatic compounds with Silica Sulphuric acid/ $NaHSO_4$ as a novel heterogeneous catalyst have been successfully developed with a good yield. The method offers aromatic sulphonic acids at ambient temperature, in higher yields and with using simplified workup procedures. The present heterogenous acid catalyst was also found to be reusable for successive runs.

## CONCLUSION

The present work offers an energy efficient and cleaner method for the synthesis of aromatic sulphonic acids, which avoids the use of excess of conc. Sulphuric acid. The procedure can be carried out at room temperature and involves simpler workup of the reaction. This results in the reaction conditions for aromatic sulphonation being milder and the process being more eco-friendly.

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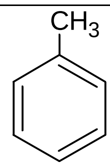
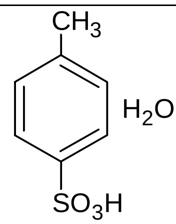
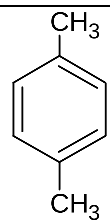
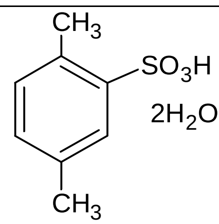
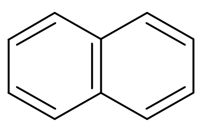
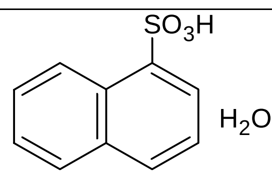
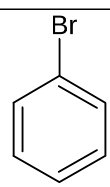
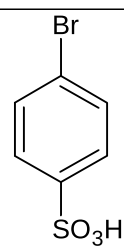
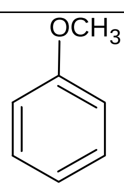
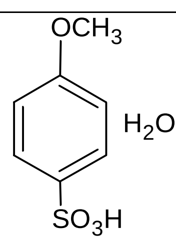
**Table 1: Silica sulphuric acid/NaHSO4 mediated aromatic sulphonation**

| Entry | Substrate | Product | Yield % | Melting Points ($^0$C) |
|---|---|---|---|---|
| 1 |  |  | 75 | 99-103 |
| 2 |  |  | 68 | 88-90 |
| 3 |  |  | 74 | 78-80 |
| 4 |  |  | 66 | 103-105 |
| 5 |  |  | 72 | 86-88 |

a: Isolated yield of 4-toluenesulphonic acid b: Reaction time : 4 hrs.

**Table 2: Reusability of catalyst for sulphonation**

| Run | Yield % [a, b] |
|---|---|
| 1 | 75 |
| 2 | 72 |
| 3 | 69 |
| 4 | 68 |
| 5 | 68 |

a: Isolated yield of 4-toluenesulphonic acid b: Reaction time : 4 hrs

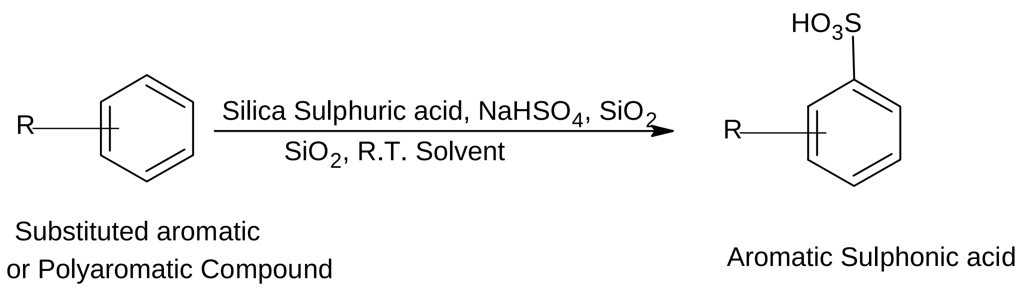



**Fig 1. Sulphonation of aromatic compounds**

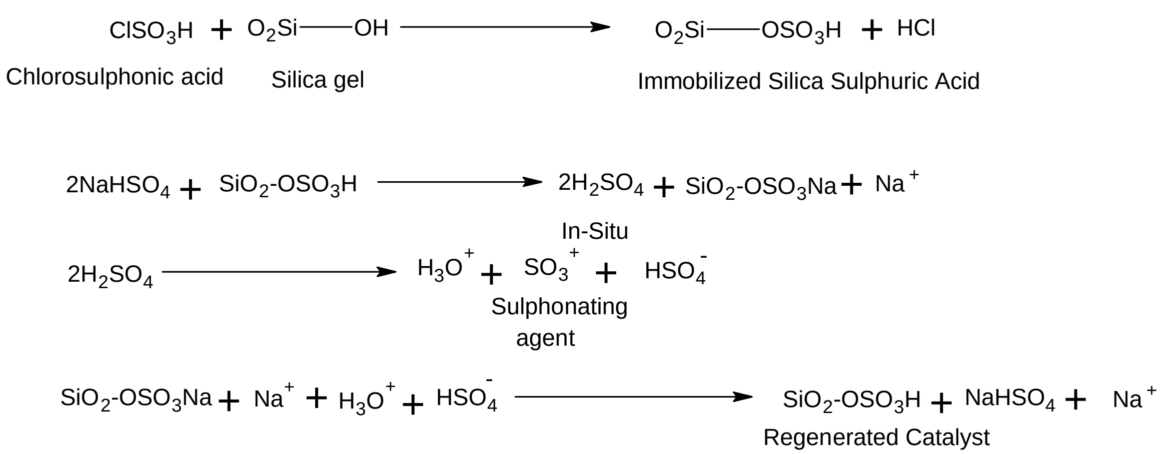



**Fig 2. In-Situ generation of Sulphonating agent from immobilized Silica Sulphuric acid**

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