

### Silica sulfuric acid (SSA): As a multipurpose catalyst

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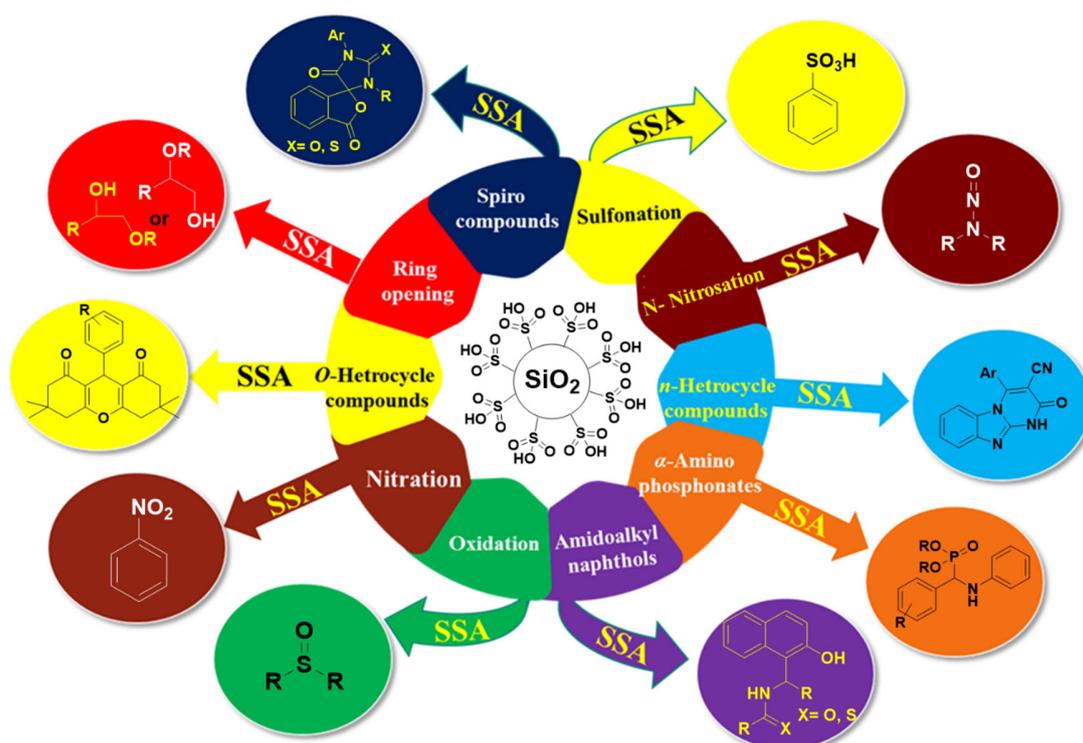


This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

### Introduction

“Green chemistry” is an important term in modern day chemical research is the chemistry which deals with the production of desired product by minimizing the application and production of hazardous substances. Catalysis is a paramount important component of green chemistry; therefore, it has become an important challenge for the chemists throughout the world to design and use of environmentally benign catalysts. Catalysis is the process of increasing the rate of a chemical reaction by adding a substance known as a catalyst, which is not consumed in the catalyzed reaction and can continue to act repeatedly. Because of this, only very small amounts of catalyst are required to alter the reaction rate in principle. In general, chemical reactions occur faster in the presence of a catalyst because the catalyst provides an alternative reaction pathway with a lower activation energy than the non-catalyzed reaction mechanism. Catalysts are classified as homogeneous or heterogeneous [1]. Heterogeneous catalysis is the type of catalysis where the phase of the catalyst differs from the phase of the reactants or products, contrasts with homogeneous catalysis where the reactants, products and catalyst exist in the same phase. Heterogeneous catalysis is very important due to their easy

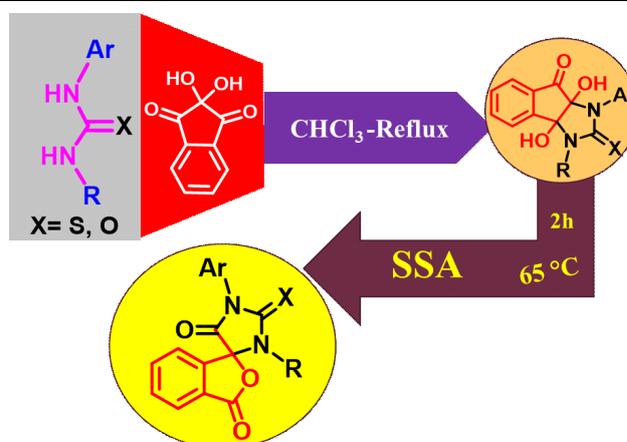
separation from reaction mixture. Among of the heterogeneous catalysts, solid acid catalysts in contrasts of liquid and homogeneous ones, are easier to handle because they hold the acidity internally and are easily separated from products by simple filtration. Moreover, constraining a reaction to the surface of a solid habitually allows one to apply milder reaction conditions [2]. Silica sulfuric acid (SSA) as a useful heterogeneous solid acid firstly, had been synthesized and introduced by Zolfigol in 2001 [3]. Silica sulfuric acid (SSA) successfully used as an efficient heterogeneous catalyst for many organic functional groups interconversions and acid catalyzed organic synthesis due to different factors such as ease of preparation, low cost, recycling and eases of handling [4]. Herein, the role of silica sulfuric acid (SSA) as a catalyst in the synthesis of various organic compounds such as, spiro compounds, *N*-heterocycle compounds, *O*-heterocycle compounds,  $\alpha$ -amino phosphonates and amidoalkyl naphthols, also for oxidation of sulfides, nitration of aromatic compounds, sulfonation of aromatic compounds, *N*-nitrosation and ring opening of epoxides has been studied. The role of SSA in organic synthesis have been comprehensively reviewed [5-7].



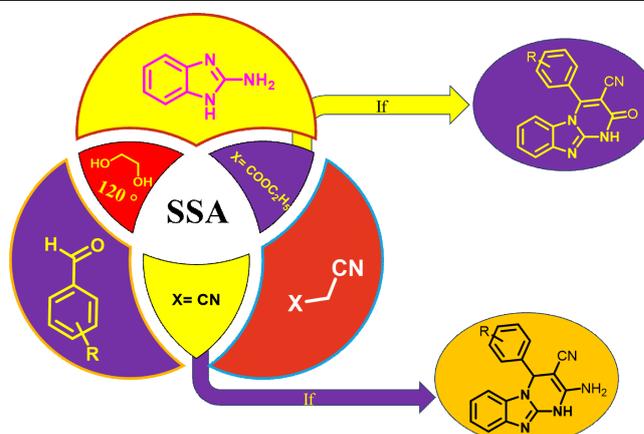
**Scheme 1.** Application of silica sulfuric acid (SSA) in the synthesis of organic compounds.

## Abstracts

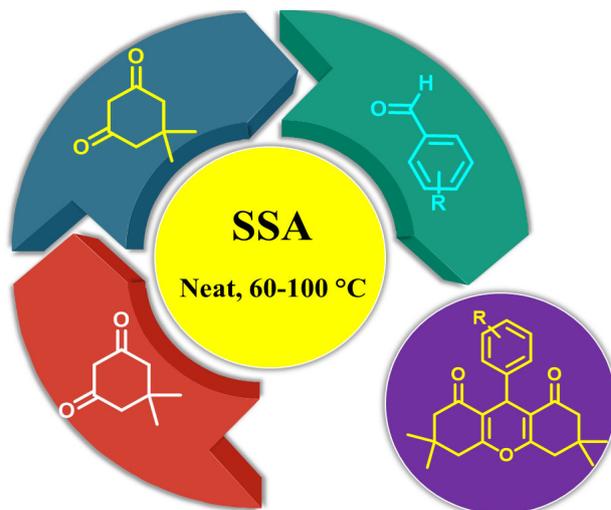
(A) In 2020, Mandal *et al.* have introduced an artificial one-pot method for syntheses spiro compounds from raw materials is easily in a short period of time using SSA catalyst. The acidic properties of SSA cooperatives have been used successfully in the easy synthesis of these compounds with diverse properties. The catalytic properties of SSA include the synthesis of spiro compounds, excellent yields of target molecules, wider substrate range, shorter reaction time and high atom economy. The multi-component domino reaction has attracted the attention of many artificial organic chemists in recent years [8].



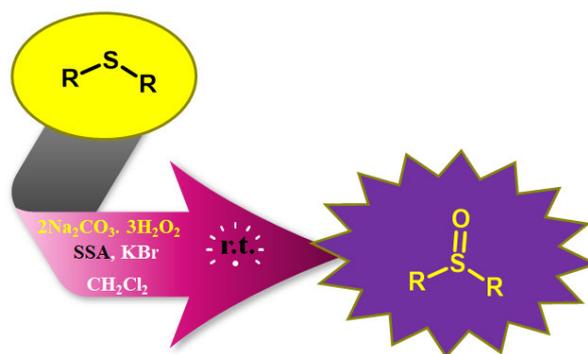
(B) In another exploration, a simple and environmentally efficient method for the synthesis of new benzo [4,5] imidazo [1,2-*a*] pyrimidine-3-carbonitrile derivatives has been performed using silica sulfuric acid/ethylene glycol catalyst. The desired compounds have been obtained by the reaction of 2-aminobenzimidazole, aldehydes and activated nitrites (malononyl or ethyl cyanostate). Silica sulfuric acid/ethylene glycol catalyst offer several advantages such as simplicity, mild reaction conditions, high yields and little environmental impact [9].



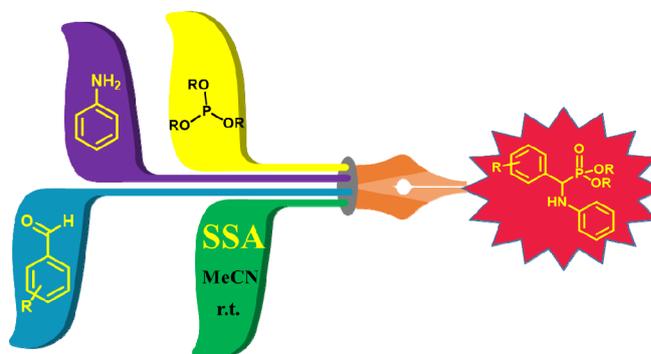
(C) In 2015, silica sulfuric acid (SSA) has been used as an efficient heterogeneous recyclable catalyst between dicton materials and aldehydes for knoevenagel compaction. 9-Aryl-1,8-dioxo-octahydroxanthene derivatives have been synthesized via a one-pot reaction in the presence of catalytic amounts of SSA under solvent-free condition. [10].



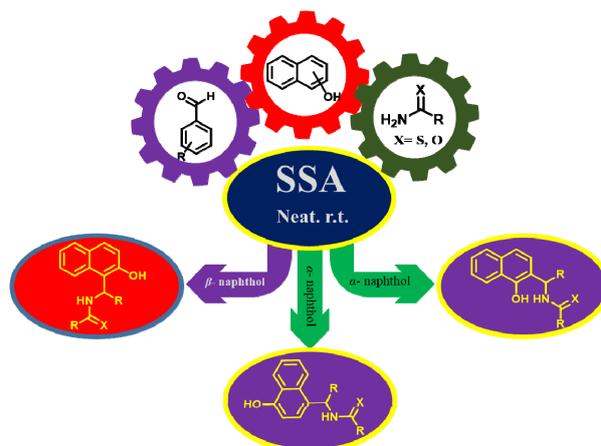
(D) Silica sulfuric acid (SSA) has been used an efficient catalyst in the selective oxidation of sulfides to sulfoxides under mild and heterogeneous conditions with moderate to good yields. Habibi *et al.* proposed this method in 2009. In this method, the oxidation of sulfides to sulfoxides has been carried out using sodium perborate and /or sodium percarbonate and silica sulfuric acid in the presence of a catalytic amount of KBr. In addition, the proposed method offers several advantages such as readily available and stable substrates, low-cost catalyst, high to excellent performance, short reaction times and simple post-treatment methods [11].



(E) Maghsoodlou *et al.* have described an efficient method for the synthesis of  $\alpha$ -amino phosphonates using silica sulfuric acid (SSA) as a heterogeneous catalyst. Mild reaction conditions, tolerance of a wide range of functional groups, and formation of desired products are the main features of described method compared to methods known for the synthesis of these compounds.  $\alpha$ -Amino phosphonates were obtained in an one-pot, simple and efficient method from the reaction between aldehyde, aniline, trialkyl phosphite and silica sulfuric acid as a catalyst in acetonitrile at room temperature [12].



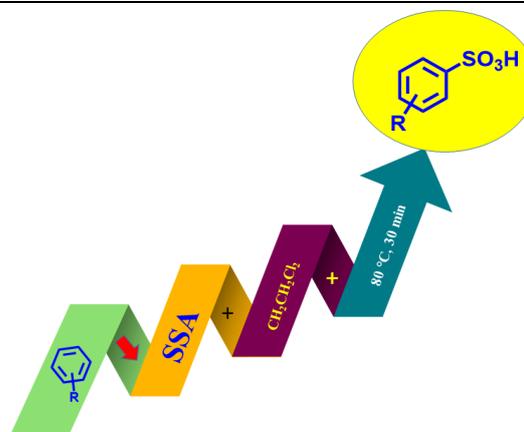
(F) In 2007 Srihari *et al.* have introduced silica sulfuric acid (SSA) as an efficient catalyst for the preparation of amidoalkyl naphthols *via* aliphatic or aromatic aldehydes, naphthol and an amide, urea or thiourea under solvent-free reaction conditions. High yields and very short reaction times are the major advantages of the reported methodology. It was found that the mentioned reported method is much more effective than the previously reported ones, due to using of SSA during reaction. Since the SSA catalyst is inexpensive, easy to install and controllable and easily portable, the described method seems to be suitable for large-scale operations [13].



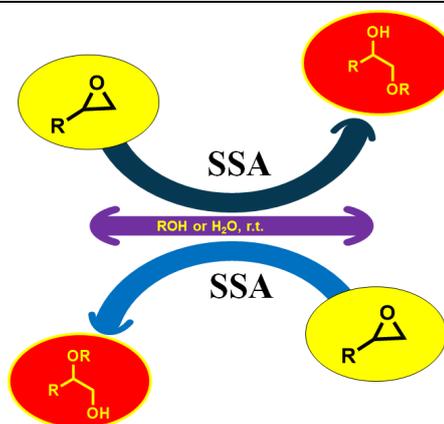
(G) Nitration of organic compounds has long been a very active and rewarding area of research. In 2004, SSA has been used as an efficient catalyst for regio and stereoselective nitration from a wide range of aromatic compounds. This work reveals a novel and efficient approach for the preparation of nitroaromatic compounds. The obtained products are interesting bioactive compounds, which they had been prepared in excellent yields and very short reaction times [14].



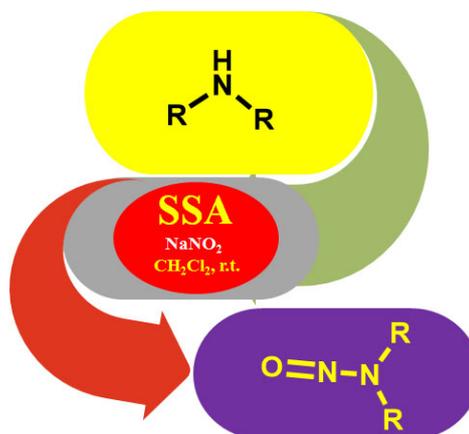
(H) The catalytic activity of silica sulfuric acid (SSA), as a heterogeneous, highly efficient, reusable, inhibitory and mild green catalyst in sulfonation of aromatic rings, has been also investigated. The sulfonation of aromatic compounds are very important due to various application of sulfonic acid derivatives. The major advantages of the described green synthesis, short reaction times and excellent yields of products. Sulfonation of the aromatic compound in this proposed method has been carried out by using silica sulfuric acid in 1,2 dichloroethane at 80 °C for 30 min [15].



(I) In another exploration, the catalytic activities of the silica sulfuric acid (SSA) has been studied as an efficient catalyst for the regioselective ring opening of epoxides by alcohols and water. The reaction of epoxides with primary, secondary and tertiary alcohols in the presence of silica sulfuric acid has been produced the corresponding  $\beta$ -alkyloxy alcohols in good to excellent yields with a high chemoselectivity. The obtained products are interesting bioactive candidates and  $\beta$ -alkoxy alcohols constitute an important class of organic compounds [16].



(J) *N*-Nitrosation chemistry of amines is an important and well established reaction in organic synthesis. These compounds are also useful synthetic intermediates for the preparation of various *N,N*-bonded functionalities. *N*-Nitrosoamines have received much attention due to their strong mutagenicity and their carcinogenicity. They have been widely studied in the medical science. In 2002, Zolfigol *et al.* have introduced the novel heterogeneous system for the chemoselective *N*-nitrosation of secondary amines under mild conditions by using silica sulfuric acid and sodium nitrite in the presence of wet SiO<sub>2</sub> [17].



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