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Chlorosulfonic acid: A high potential reagent in catalyst design

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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.

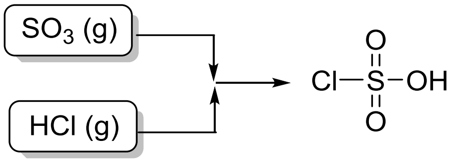
Introduction

Chlorosulfonic acid was first prepared by Williamson in 1854 [1]. Chlorosulfonic acid ($ClSO_3H$) is a colourless or straw-coloured liquid which fumes in air and decomposes slightly at its boiling point (151-152°C) [2]. It is a strong acid which is toxic and corrosive and behaves as a dehydrating, oxidizing and chlorinating agent. It is soluble in some organic solvents, such as: $CHCl_3$, CH_2Cl_2, CH_3COOH, acetic anhydride and nitrobenzene. Chlorosulfonic acid may be stored and transported in steel containers, but in this case the iron content will be in the range 25-50 ppm [3]. Many reports showed that chlorosulfonic acid could act as a catalyst in some important reactions such as: esterification of aliphatic alcohols, alkylation of alkenes, and synthesis of alkyl halides from alkenic halides and isoalkanes containing tertiary hydrogen. Meanwhile, it was a powerful acid with a high reactivity because of its relatively weak sulfurchlorine (S-Cl) bond. This property led to that this reagent used for designing of various acidic catalysts.

It is also used as a vulcanization accelerator, a source of anhydrous hydrogen chloride and in the tanning, textile and paper industries [4].

Preparation

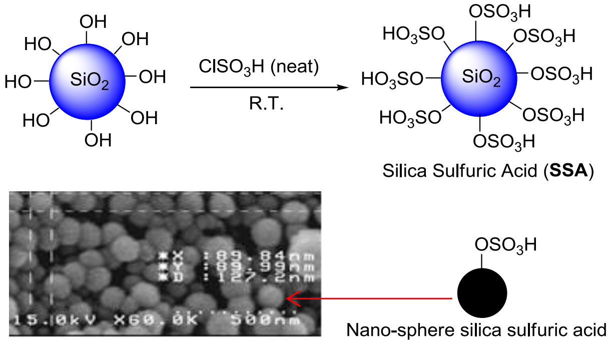
Chlorosulfonic acid is commercial available but can also be readily prepared from direct action of hydrogen chloride on sulfur trioxide and by passing a vigorous stream of hydrogen chloride into fuming sulfuric acid (Scheme 1) [2].



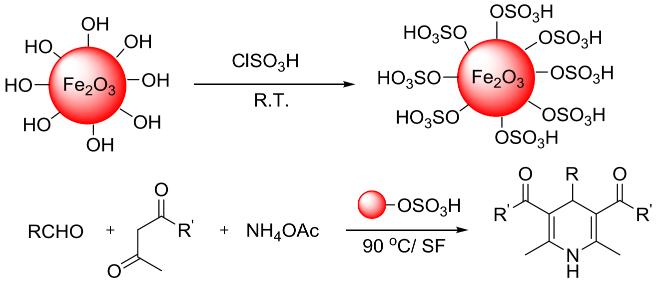
Scheme 1. Preparation of chlorosolfonic acid

Abstracts

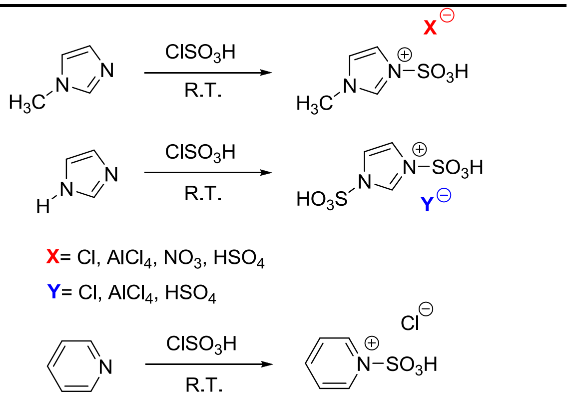
(A) Synthesis of silica sulfuric acid (SSA) as an acidic resin. Zolfigol reported silica based acidic resin namely silica sulfuric acid (SSA) *via* reaction of neat chlorosulfonic acid with silica gel for the first time [5] The SSA is a unique heterogeneous acidic catalyst and has been used widely in organic functional group transformation [6]. It should be mentioned that SSA used in over 300 research papers so far. Recently, they reported a new developed model of SSA in nano scale (between 60 and 90 nm) [7].



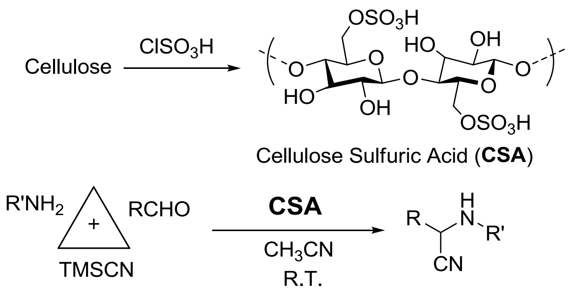
(B) Design an acidic nano magnetic particle [sulfonic acid supported γ-Fe_2O_3 {Fe_2O_3-SO_3H}]. At 2012, a magnetic particle-supported sulfonic acid catalyst was prepared for the first time by Zolfigol and co-workers [8]. These particles were prepared immediately with a low cost procedure and had several positive points such as; High activity in Hantzsch synthesis, high reusability (over 5 runs), stable and high densities of functional groups. After this report, Fe_3O_4-SO_3H (magnetite nanocatalyst) was also prepared at 2013 by Gawande [9].



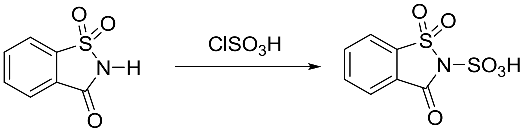
(C) Sulfonic acid functionalized imidazolium salts (SAFIS). Sulfonic acid functionalized imidazolium salts were synthesized by loaded sulfonic acid groups on 1-methyl imidazole and imidazole and produced new family of ionic liquids with amazing properties. These ILs were successfully employed as catalysts in several organic transformations [10]. In continues of this research, synthesis of 1-sulfopyridinium chloride as a new, homogeneous and reusable catalyst was reported [11].



(D) Synthesis of a *bio*-supported catalyst. Cellulose as a very cost-effective and biodegradable compound was converted to their sulfonic acid derivative by the reaction with $ClSO_3H$ to give cellulose sulfuric acid (CSA). CSA showed catalytic properties and *α*-Amino nitriles are synthesized by a one-pot three-component condensation reaction of amines, aldehydes and trimethylsilylcyanide in the presence of a catalytic amount of it as a *bio*-supported catalyst [12].

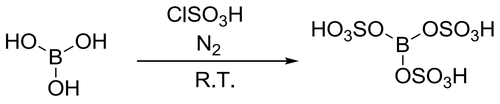


(E) Saccharin sulfonic acid. Reaction of chlorosulfonic acid with saccharin was designed by Shirini and yielded a bio-supported and recyclable solid acid catalyst. Several reactions were catalyzed by it such as Chemoselective trimethylsilylation of alcohols [13], preparation and deprotection of 1,1-diacetates [14] and N-Boc protection of amines and formation of tertbutyl ethers from alcohols [15].



Saccharin Sulfonic Acid (**SaSA**)

(F) Boron Sulfonic Acid. Boron sulfonic acid (BSA) was introduced by Kiasat and co-workers as a strong acidic catalyst and used it for the regioselective ring opening of epoxides to β-hydroxy thiocyanates in the presence of BSA by NH_4SCN in a solvent less media. The promising points for the presented methodology were efficiency, generality, high yield, relatively short reaction time, cleaner reaction profile, ease of product isolation, simplicity, and finally compliance with the green chemistry protocols [16].



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