

SYNLETT Spotlight 318

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

Silica-Functionalized Sulfonic Acid

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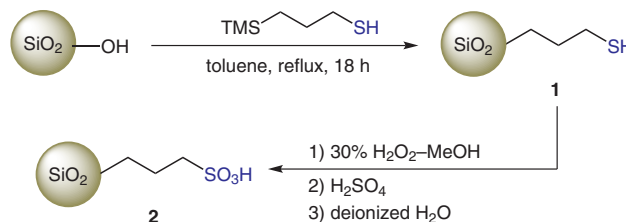


Introduction

Polymer-supported catalysts have been widely used in research and in process chemistry due to the easy recovery, high stability, activity, and selectivity. However, their use is restricted because of the easy damage to the organic polymer backbone (thermal or chemical).¹ One way to overcome this problem of the traditional polymer-supported catalysts is to change the expensive organic polymer chain to a silica chain having a covalently anchored organic spacer to create organic–inorganic hybrid (interphase) catalysts.² In these type of solid acids the reactive centers are highly mobile like homogeneous catalysts and at the same time there is the advantage of recyclability of the heterogeneous catalysts. One of these silica-supported catalysts, silica-functionalized sulfonic acid (SFSA), has been widely used in research and in process chemistry due to its easy recovery, light efficiency, recyclability, and stability.¹

Preparation

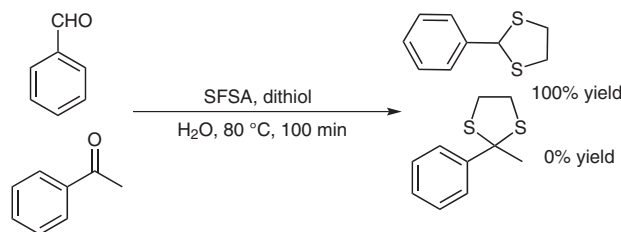
Mesoporous amorphous silica gel was activated by refluxing in concentrated hydrochloric acid and then washed thoroughly with deionized water and dried before undergoing chemical surface modification. After refluxing the activated silica gel with 3-mercaptopropyltrimethoxysilane, the solid materials were filtered off and washed and then dried to give the surface-bound thiol group.³ The thiol groups of the modified silica were oxidized with a 30% H₂O₂ solution and concentrated H₂SO₄ in methanol and the solid was filtered off and washed with deionized water. To ensure that all the sulfonic acid groups were protonated, the solid was suspended, filtered and washed thoroughly with deionized water and dried overnight.



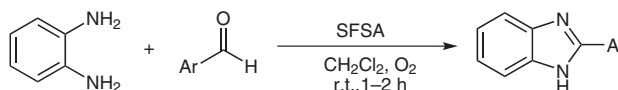
Scheme 1 Preparation of silica-functionalized sulfonic acid (SFSA)

Abstracts

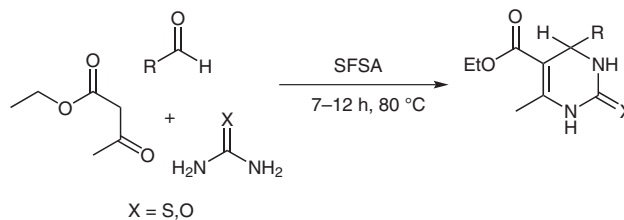
(A) Karimi and Khalkhali have reported the efficient and highly chemoselective thioacetalization of carbonyl compounds using a dithiol in the presence of a catalytic amount of SFSA.³



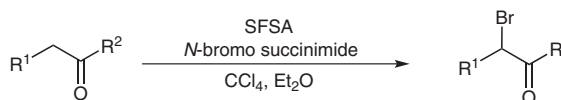
(B) Das and co-workers used SFSA for the synthesis of benzimidazoles starting from *O*-phenylenediamine and aromatic and aliphatic aldehydes.⁴



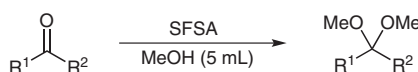
(C) SFSA catalyzed the one-pot synthesis of 3,4-dihydropyrimidinones/thiones under heterogeneous conditions. The catalyst was found to be completely heterogeneous and also reusable for several times without significant loss of activity.⁵



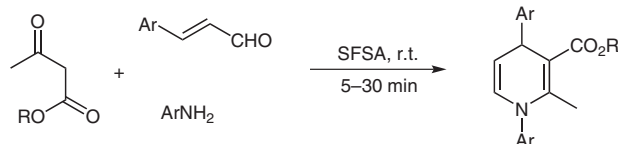
(D) A wide range of carbonyl compounds were transformed into the corresponding monobrominated products by using *N*-bromo succinimide in the presence of SFSA.⁶



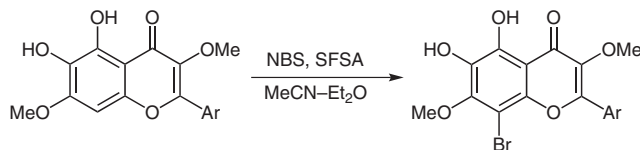
(E) Smooth transformations of a wide range of aldehydes and ketones into the corresponding acetals were occurred by using SFSA under mild and simple reaction conditions.⁷



(F) Three-component Hantzsch-type reactions can be performed using SFSA under solvent-free conditions. The conversions proceeded at room temperature, within a short reaction time and the products were formed in high yields.⁸



(G) A series of phenols, alkoxy arenes, and anilines were converted into the corresponding monobromo compounds (*ortho* and *para*) in high yields and within short reaction times in the presence of *N*-bromo succinimide and SFSA.⁹



References

- (1) Sherrington, D. C. *Polymer-Supported in Synthesis*, In *Chemistry of Waste Minimization*; Clark, J. H., Ed.; Blackie Academic: London, **1995**, 141–200.
- (2) (a) Lu, Z. L.; Lindner, E.; Mayer, H. A. *Chem. Rev.* **2002**, *102*, 3543. (b) Wight, A. P.; Davis, M. E. *Chem. Rev.* **2002**, *102*, 3589. (c) Clark, J. H.; Macquarrie, D. J. *Chem. Commun.* **1998**, 853.
- (3) Karimi, B.; Khalkhali, M. *J. Mol. Catal. A: Chem.* **2007**, *271*, 75.
- (4) Das, B.; Kanth, B. S.; Reddy, K. R.; Kumar, A. S. *J. Heterocycl. Chem.* **2008**, *45*, 1499.
- (5) Gupta, R.; Paul, S.; Loupy, A. *J. Mol. Catal. A: Chem.* **2006**, *266*, 50.
- (6) Das, B.; Venkateswarlu, K.; Holla, H.; Krishnaiah, M. *J. Mol. Catal. A: Chem.* **2006**, *253*, 107.
- (7) Shimizu, K.; Hayashi, E.; Hatamachi, Y.; Kodama, T.; Kitayama, Y. *Tetrahedron Lett.* **2004**, *45*, 5135.
- (8) Das, B.; Suneel, K.; Venkateswarlu, K.; Ravikanth, B. *Chem. Pharm. Bull.* **2008**, *56*, 366.
- (9) Das, B.; Venkateswarlu, K.; Krishnaiah, M.; Holla, H. *Tetrahedron Lett.* **2006**, *47*, 8693.