

Silylation of Alcohols and Phenols with Hexamethyldisilazane over Highly Reusable Propyl Sulfonic Acid Functionalized Nanostructured SBA-15

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Abstract: Various alcohols and phenols were trimethylsilylated in excellent yields using hexamethyldisilazane in the presence of catalytic amounts of environmentally friendly, hydrophobic, highly thermal stable, and completely heterogeneous sulfonic acid functionalized mesostructured SBA-15 in dichloromethane at ambient temperature. Primary, bulky secondary, tertiary, and phenolic hydroxyl functional groups were transformed to the corresponding trimethylsilyl ethers in excellent yields. The simple experimental procedure was accompanied by easy recovery and the catalyst was reusable (at least 18 reaction cycles); these are attractive features of this protocol.

Key words: reusable heterogeneous catalyst; solid sulfonic acid; SBA-15; protecting group; silylation; hexamethyldisilazane

The protection of the hydroxyl function in alcohols and phenols is a common and versatile part of many syntheses of reasonable complexity. Among the routinely employed methodologies for the masking of hydroxyl groups in organic chemistry, the transformation of alcohols to the corresponding silyl ethers is a popular procedure [1,2]. The popularity and extensive use of silyl ethers as protecting groups for alcohols come from their ease of formation, resistance to oxidation, good stability toward most non-acidic reagents, and easy deprotection to provide free alcohols [3]. Although many reagents are available for the silylation of hydroxyl groups [4–13], some of these methods suffered from serious drawbacks such as the lack of reactivity, low product yields, long reaction times, expensive reagents and catalysts, and robust purification steps or difficulty in by-product removal. In contrast, 1,1,1,3,3,3-hexamethyldisilazane (HMDS) is a cheap, easy handling, commercially available and stable reagent, and it is frequently used for the trimethylsilylation of hydroxyl groups giving ammonia as the only by-product. However, the main drawback of HMDS is its poor silylating power as it needs forceful conditions and long reaction times in many instances [14]. Therefore, a variety of catalysts have been developed for the activation of this reagent such as sulfuric acid [2], $(\text{CH}_3)_3\text{SiCl}$ [15], sulfonic acids [16], K-10 montmorillonite

[17,18], iodine [19], tungstophosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) [20], LiClO_4 [21], TBBDA and PBBS [22], $[\text{PdCl}(\eta^3\text{-C}_3\text{H}_5)]_2\text{-PPh}_3$ [23], HReO_4 [24], LaCl_3 [25], tribromomelamine [26], $\text{Bi}(\text{OTf})_3$ [27], tribromoisocyanuric acid and DABCO-Br [28]. Although the silylation ability of HMDS has been improved by these methods, some problems such as the use of a corrosive catalyst, drastic reaction conditions, tedious workup, and long reaction times still need to be overcome. Moreover, many of these reagents are expensive and non-recoverable leading to the generation of a large amount of toxic waste particularly when large-scale applications are considered. In other words, the tightening of legislation with regard to the treatment and disposal of toxic waste produced during the difficult separation of the desired products is forcing industry to consider greener technologies. Therefore, solid acids catalysis is a growing field of research as the demand for clean and eco-friendly chemical processes is increasing [29–34]. Accordingly, chemical industry is currently searching for highly active, stable, and recyclable solid acids to improve the environmental safety of the production of chemicals under milder reaction conditions. To address these issues, Zareyee and Karimi [35] demonstrated the application of recoverable sulfonic acid functionalized ordered mesoporous silica (MCM-41-Pr-SO₃H) for the efficient silylation of alcohols and phenols. Quite recently, they

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used a heterogeneous and hydrophobic sulfonic acid nanoreactor with acidic sites and phenyl groups within the mesochannel of SBA-15 as an efficient, environmentally benign, and highly recoverable catalyst for the Pechmann [36] and Strecker [37] reactions. In the course of our ongoing green organic chemistry program and current interest in the development of nanostructured solid acids for different organic transformations [35–39], we report on a brief preparation and application of a sulfonic acid nanoreactor (SBA-15-Ph-Pr-SO₃H) for the trimethylsilylation of hydroxyl groups.

1 Experimental

1.1 Preparation of SBA-15-Ph-Pr-SO₃H

The synthesis of SBA-15-Pr-SH was achieved using the known procedure described by Stucky et al. [40]. This procedure involved a synthetic strategy based on the co-condensation of tetraethoxysilane (TEOS) and 3-mercaptopropyltrimethoxysilane (MPTMS) in the presence of Pluronic P123 as the structure directing agent. In a typical preparation procedure, 4 g of Pluronic P123 (Aldrich, average $M_w = 5800$) was dissolved in 125 g of 1.9 mol/L HCl solution with stirring at room temperature. The solution was heated to 40 °C before adding 6.83 g TEOS. After a 3 h pre-hydrolysis of TEOS, 1.6 g thiol precursor MPTMS was added. The resultant solution was stirred for 20 h at 40 °C after which the mixture was aged at 100 °C for 24 h under static conditions. The solid was recovered by filtration and air dried at room temperature overnight. The template was removed from the as-synthesized material by washing with ethanol using a Soxhlet apparatus for 24 h.

To a suspension of SBA-15-Pr-SH (3 g) in dry toluene PhSi(OEt)₃ (PTES, 4 mmol) was added. The resulting mixture was first stirred at room temperature for 1 h and then refluxed for a further 24 h. The solid material was filtered and successively washed with toluene, EtOH, and Et₂O and dried overnight at 120 °C to afford the corresponding SBA-15-Ph-Pr-SH.

Conversion of the catalyst's thiol groups to sulfonic acid moieties was accomplished by hydrogen peroxide. Typically, 0.3 g of solid hydrophobic material was suspended in 10 g of aqueous 30 wt% H₂O₂. This suspension was stirred at room temperature in an Ar atmosphere for 24 h. After the oxidation treatment, the resulting solution was filtered and washed separately with water and ethanol. Finally the wet material was suspended in 1 mol/L H₂SO₄ solution for 2 h and it was then washed several times with water and ethanol and dried at 60 °C under vacuum overnight to give the corresponding SBA-15-Ph-Pr-SO₃H, denoted as catalyst **1** (Fig. 1).

The concentration of sulfonic acid groups in catalyst **1** was quantitatively estimated by ion-exchange pH analysis. To an aqueous solution of NaCl (1 mol/L, 25 ml) with a primary pH of 5.1 the catalyst **1** (100 mg) was added and the resulting mixture was stirred for 6 h after which the pH of the solution

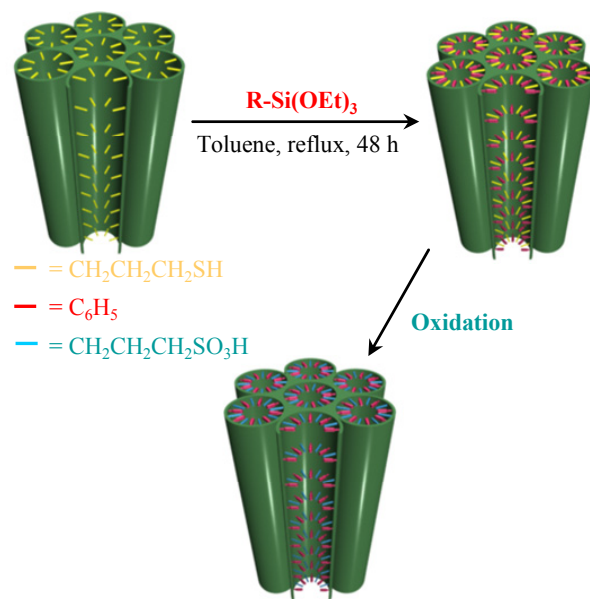


Fig. 1. Schematic representation of the preparation of the sulfonic acid based catalyst **1**.

decreased to 2.19

1.2 General procedure for the trimethylsilylation of alcohols

To a solution of alcohol (1 mmol) and HMDS (0.6 mmol) in dichloromethane (3 ml) catalyst **1** (19 mg, 3 mol%) was added. The mixture was stirred at 35 °C for a period of time (Fig. 2). Reaction progress was monitored by thin layer chromatography (TLC) and gas chromatography (GC). After the completion of the reaction the product was isolated by filtration. Evaporation of the solvent under reduced pressure gave the

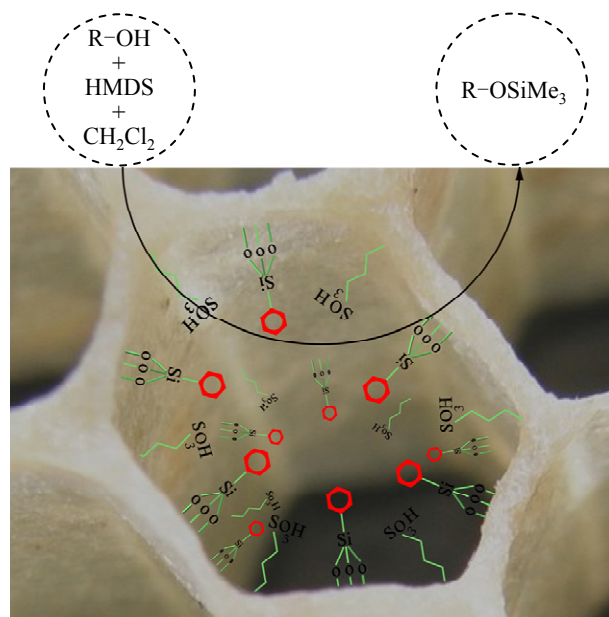


Fig. 2. Silylation reaction using catalyst **1**.

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