

Sulfuric acid ([3-(3-silicapropyl)-sulfanyl]propyl)ester as recyclable catalyst for the silylation of hydroxyl groups

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ABSTRACT

Sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl)ester (SASPSPE) is employed as a recyclable catalyst for the silylation of hydroxyl groups. A good range of primary, secondary alcohols and phenolic hydroxyl groups were effectively converted into their corresponding trimethylsilyl ethers with hexamethyldisilazane in the presence of catalytic amounts of SASPSPE at room temperature with short reaction times in good to excellent yields. This heterogeneous catalyst was recycled for nine runs without losing its catalytic activity.

Keywords: Sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl)ester, Silylation, Catalyst, Hydroxyl group, Heterogeneous solid acid

1. Introduction

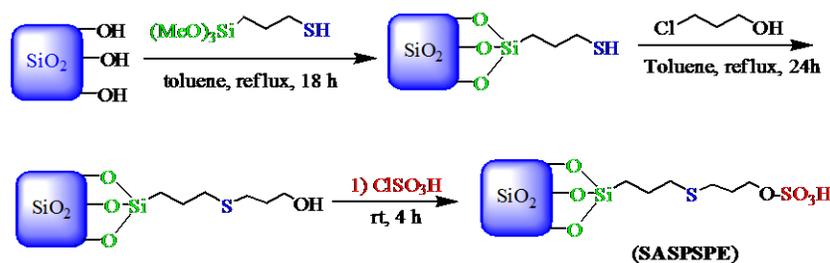
The development of heterogeneous catalysis is an important area in organic synthesis as it provides not only an alternative to homogeneous catalysis but also has the advantages of easy catalyst recovery, recycling, mild reaction condition. Solid acid catalysis is a growing field of research as the demand for clean and eco-friendly chemical processes is increasing [1-4].

Several types of solid sulfonic acid functionalized silica (both amorphous and ordered) have been synthesized and applied as an alternative to traditional sulfonic acid resins and homogeneous acids in catalyzing chemical transformations [5,6]. In continuation of our studies on the design and application of solid acid catalysts in organic transformations [5-9], herein, we describe the application of sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl)ester (SASPSPE) as recyclable catalyst for the silylation of hydroxyl groups under mild conditions (Scheme 1).

The protection of hydroxyl function in alcohols and phenols is a common and versatile event in many syntheses of reasonable complexity and among the routinely employed methodologies for the masking of hydroxyl groups in organic chemistry, transformation of alcohols to the corresponding silyl ether represents one of the most popular procedures [10]. It is well known that the popularity and

extensive use of silyl ethers as protecting groups for alcohols result from their ease of formation, resistance to oxidation, good stability for most non-acidic reagents and easily deprotection to provide the free alcohols [11]. Although many reagents are available for the silylation of hydroxyl groups [12-16], some of these methods suffered from serious drawbacks such as lack of reactivity, low yields of products, long reaction times, expensive reagents and catalysts, robust purification step or the difficulty in removal of by-products. In contrast, 1,1,1,3,3,3-hexamethyldisilazane (HMDS) as a cheap, easy handling, commercially available and stable reagent, is frequently used for trimethylsilylation of hydroxyl groups, giving ammonia as the only by-product. However, the main drawback of HMDS is its poor silylating power which needs forceful condition and long reaction times in many instances [17]. Therefore, a variety of catalysts have been developed for the activation of HMDS in the literature such as: trichloroisocyanuric acid (TCCA) [18], tungstophosphoric acid [19], K-10 montmorillonite [20], lithium perchlorate [21], cupric sulfate pentahydrate [22], H- β -zeolite [23], MgBr₂.OEt₂ [24], silica supported perchloric acid [25], alumina sulfuric acid [26], sulfonic acid-functionalized environmentally safe disposal [27], silica sulfuric acid [28], tribromomelamine [29], 1,3-dibromo-5,5-diethylbarbituric acid [30], tribromoisocyanuric acid and DABCO-Br₂ [31], ZrO(OTf)₂ [32], tetrabutylammonium bromide [33], silica supported tin chloride [34], silica-bonded S-sulfonic acid [35], {[K.18-crown-6]I₃]_n [36], tetrabutylammonium

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Scheme 1. Preparation of sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl)ester (SASPSPE).

phthalimide-N-oxyl [37], and cross-link poly(vinylpyridine/styrene)copolymer-supported bismuth (III) triflate [38].

2. Experimental

General: Chemicals were purchased from Merck, Fluka and Aldrich Chemical Companies. IR spectra were run on a Shimadzu Infra Red Spectroscopy IR-435. The ^1H NMR was run on JEOL NMR- Spectrometer FX 90Q and Bruker Avance (DRX 500 MHz). Melting points were recorded on a Melting Point SMP1 apparatus in open capillary tubes and are uncorrected. With TLC using silica gel SILG/UV 254 plates the progress of reaction was followed. All of the products are known and characterized by comparison of their spectral (IR, ^1H -NMR), TLC and physical data with those reported in the literature [18-38].

2.1. Catalyst Preparation:

2.1.1. 3-(3-Silicapropylthio)-1-propanol

3-Chloro-1-propanol (5 mmol, 0.473 g) was added to a magnetically stirred mixture of 3-mercaptopropylsilica (10 g) in toluene (30 mL), then some drops of triethyl amine was added and the resulting mixture refluxed for 24 h. The mixture was filtered and the solid was washed with ethanol (3×20 mL), and then dried in an oven. 3-(3-Silicapropylthio)-1-propanol was obtained as a cream powder (10.3 g).

2.1.2. Sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl)ester

To a mixture of 3-(3-silicapropylthio)-1-propanol (5 g) in chloroform (20 mL), chlorosulfonic acid (0.19 g, 1.65 mL) was added dropwise at 0°C during 2 h. After addition was complete, the mixture was stirred for 2 h until HCl gas evolution was stopped. Then, the mixture was filtered and washed with ethanol (30 mL) and dried at room temperature to obtain sulfuric acid ([3-(3-silicapropyl) sulfanyl] propyl)ester as a cream powder (5.13 g). Sulfur content of the samples by conventional elemental analysis was 15.51% [7a].

2.1.3. General procedure for the silylation of hydroxy groups

To a stirred solution of compound containing hydroxyl group (1 mmol) and HMDS (0.8 mmol) in CH_3CN (2 mL)

was added SASPSPE (0.015 g, 0.5 mol%) and stirred at room temperature. When the reaction was complete by GC (or TLC, n-hexane-EtOAc, 9:1) analysis, CH_2Cl_2 was added (10 mL), and SASPSPE was removed by filtration. The solvent was evaporated and the trimethylsilyl ether was isolated almost as a pure crude product. Further purification was carried out by short column chromatography on silica gel eluting with ethyl acetate/petroleum ether, if necessary.

The Selected spectral data:

Trimethyl(benzyloxy)silan (Table 3, entry 1) Purified on short column of silica gel using petroleum ether/ ethyl acetate (10:1) as eluent; Colorless liquid; bp $212^\circ\text{C}/760$ torr; ^1H NMR (500 MHz, CDCl_3 , ppm) δ : 0.19 (s, 9H), 4.72 (s, 2H), 7.35-7.36 (m, 5H).

Trimethyl(4-methoxybenzyloxy)silan (Table 3, entry 2) Purified on short column of silica gel using petroleum ether/ ethyl acetate (10:1) as eluent; Colorless liquid; bp 257 - $258^\circ\text{C}/760$ torr; ^1H NMR (500 MHz, CDCl_3 , ppm) δ : 0.18 (s, 9H), 3.81 (s, 3H), 4.66 (s, 2H), 6.91 (d, 2H, $J = 8.5$ Hz), 7.44 (d, 2H, $J = 8.4$ Hz). ^{13}C NMR (125 MHz, CDCl_3 , ppm) δ : 0.30, 55.21, 64.41, 113.75, 128.13, 133.16, 158.90.

Trimethyl(4-fluorophenoxy) silan (Table 3, entry 5) Purified on short column of silica gel using petroleum ether/ ethyl acetate (10:1) as eluent; Colorless liquid; bp $208^\circ\text{C}/760$ torr; ^1H NMR (500 MHz, CDCl_3 , ppm) δ : 0.25 (s, 9H), 6.75-6.77 (m, 2H), 6.89-6.92 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3 , ppm) δ : 0.53, 116.10, 121.26, 151.52, 159.08.

Table 1. Conversion of benzyl alcohol to the corresponding silylether with HMDS in the presence of different amounts of catalyst SASPSPE.^a

Entry	Catalyst loading (g)	Time (min)	Conversion (%)
1	No catalyst	105	100
2	0.005	35	100
3	0.01	20	100
4	0.015	4	100
5	0.02	4	100

^aReaction conditions: benzyl alcohol (1 mmol), HMDS (0.8 mmol), room temperature, acetonitrile.

Table 2. The effect of solvents on the silylation of benzyl alcohol with HMDS in the presence of catalyst SASPSPE. ^a

Entry	Solvent	Time (min)	Conversion (%)
1	n-Hexane	180	70
2	Acetonitrile	4	100
3	Ethyl acetate	180	90
4	Dichloromethane	180	80
5	Diethyl ether	180	55
6	Chloroform	180	20
7	Acetone	180	60

^aReaction conditions: benzyl alcohol (1 mmol), HMDS (0.8 mmol), room temperature, Cat. SASPSPE (0.015 g).

Trimethyl(4-nitrobenzyloxy)silan (Table 3, entry 6) Purified on short column of silica gel using petroleum ether/ ethyl acetate (10:1) as eluent; Colorless liquid; bp >300 °C/760 torr; ¹H NMR (500 MHz, CDCl₃, ppm) δ: 0.22 (s, 9H), 4.83 (s, 2H), 7.52 (d, 2H, *J* = 8.8 Hz), 8.22 (d, 2H, *J* = 8.7 Hz). ¹³C NMR (125 MHz, CDCl₃, ppm) δ: -0.10, 63.95, 123.95, 127.00, 147.49, 149.16.

Trimethyl(3-phenylpropyloxy)silan (Table 3, entry 9) Purified on short column of silica gel using petroleum ether/ ethyl acetate (10:1) as eluent; Colorless liquid; bp 245 °C/760 torr; ¹H NMR (500 MHz, CDCl₃, ppm) δ: 0.22 (s, 9H), 1.92-1.98 (m, 2H), 2.77 (t, 2H, *J* = 7.8 Hz), 3.70 (t, 2H, *J* = 6.4 Hz), 7.26-7.29 (m, 3H), 7.35-7.38 (m, 2H). ¹³C NMR (125 MHz, CDCl₃, ppm) δ: 0.03, 32.60, 34.70, 62.36, 126.17, 128.75, 128.91, 142.58.

Trimethyl(diphenylmethoxy)silan (Table 3, entry 11) Purified on short column of silica gel using petroleum ether/ ethyl acetate (10:1) as eluent; Colorless liquid; bp >300 °C/760 torr; ¹H NMR (500 MHz, CDCl₃, ppm) δ: 0.20 (s, 9H), 5.88 (s, 1H), 7.32 (t, 2H, *J* = 7.3 Hz), 7.40 (t, 4H, *J* = 7.6 Hz), 7.46 (t, 4H, *J* = 7.5 Hz). ¹³C NMR (125 MHz, CDCl₃, ppm) δ: 0.65, 77.00, 127.04, 127.53, 128.68, 145.35.

Trimethyl(1-phenyl-2-methyl-2-propyloxy) silan (Table 3, entry 13) Purified on short column of silica gel using petroleum ether/ ethyl acetate (10:1) as eluent; Colorless liquid; bp 245 °C/760 torr; ¹H NMR (90 MHz, CDCl₃, ppm) δ: 0.05 (s, 9H), 1.20 (s, 6H), 2.71 (s, 2H), 7.12-7.38 (m, 5H).

Trimethyl[1-methyl-1-(4-methyl-cyclohex-1-enyl) ethoxy] silan (Table 3, entry 14) Purified on short column of silica

gel using petroleum ether/ ethyl acetate (10:1) as eluent; Colorless liquid; bp 256 °C/760 torr; ¹H NMR (90 MHz, CDCl₃, ppm) δ: 0.09 (s, 9H), 0.94-2.00 (m, 16H), 5.27-5.44 (m, 1H).

Trimethyl(biphenyl-2-yloxy) silan (Table 3, entry 16) Purified on short column of silica gel using petroleum ether/ ethyl acetate (10:1) as eluent; Colorless liquid; bp 281 °C/760 torr; ¹H NMR (500 MHz, CDCl₃, ppm) δ: 0.05 (s, 9H), 6.92 (dd, 1H, *J*₁ = 8.0 Hz, *J*₂ = 0.7 Hz), 7.06 (dt, 1H, *J*₁ = 7.5 Hz, *J*₂ = 0.8 Hz), 7.21-7.26 (m, 1H), 7.31 (t, 1H, *J* = 7.4 Hz), 7.36 (dd, 1H, *J*₁ = 7.5 Hz, *J*₂ = 1.5 Hz), 7.40 (t, 2H, *J* = 7.5 Hz), 7.54 (d, 2H, *J* = 8.3 Hz). ¹³C NMR (125 MHz, CDCl₃, ppm) δ: 0.51, 121.03, 122.35, 127.16, 128.26, 128.81, 130.06, 133.78, 139.49, 152.73.

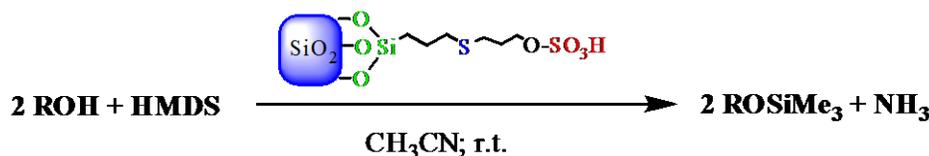
Trimethyl(2-naphtaleneoxy)silan (Table 3, entry 18) Purified on short column of silica gel using petroleum ether/ ethyl acetate (10:1) as eluent; Colorless liquid; bp 282 °C/760 torr; ¹H NMR (500 MHz, CDCl₃, ppm) δ: 0.41 (s, 9H), 7.18 (dd, 1H, *J*₁ = 8.8 Hz, *J*₂ = 2.3 Hz), 7.31 (d, 1H, *J* = 2.1 Hz), 7.41 (t, 1H, *J* = 7.3 Hz), 7.50 (dt, 1H, *J*₁ = 7.6 Hz, *J*₂ = 0.8 Hz), 7.77-7.85 (m, 3H).

Trimethyl(2,4,6-trimethylphenoxy)silan (Table 3, entry 19) Purified on short column of silica gel using petroleum ether/ ethyl acetate (10:1) as eluent; Colorless liquid; bp 241 °C/760 torr; ¹H NMR (500 MHz, CDCl₃, ppm) δ: 0.25 (s, 9H), 2.17 (s, 6H), 2.23 (s, 3H), 6.78 (s, 2H). ¹³C NMR (125 MHz, CDCl₃, ppm) δ: 1.37, 18.02, 20.94, 128.51, 129.47, 130.70, 150.63.

Trimethyl(4-aminophenoxy)silan (Table 3, entry 21) Purified on short column of silica gel using petroleum ether/ ethyl acetate (10:1) as eluent; Colorless liquid [25]; ¹H NMR (500 MHz, CDCl₃, ppm) δ: 0.22 (s, 9H), 3.34 (s, 2H), 6.51 (d, 2H, *J* = 8.5 Hz), 6.61 (d, 2H, *J* = 8.5 Hz).

3. Results and Discussion

To study the effect of catalyst loading on the protection of hydroxyl group as the corresponding silylether the reaction of benzyl alcohol with HMDS was chosen as a model reaction (Table 1). As shown in Table 1, the optimal amount of SASPSPE was 0.015 g per 1 mmol of benzyl alcohol and 0.8 mmol of HMDS. The model reaction was also examined in various solvents in the presence of 0.015 g (0.5 mol%) of SASPSPE (Table 2). The results in Table 2 show that amongst these solvents, acetonitrile was the solvent of choice in terms of reaction time and product yield.



Scheme 2. SASPSPE catalyzed silylation of hydroxyl groups.

Table 3. Silylation of alcohols and phenols with HMDS in the presence of SASPSPE as catalyst at room temperature.

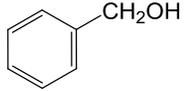
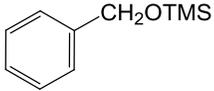
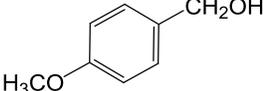
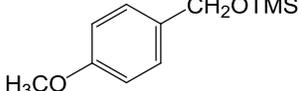
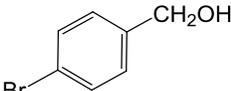
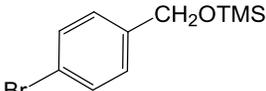
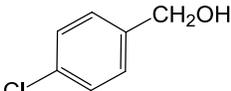
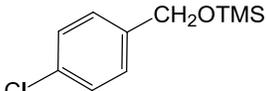
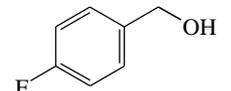
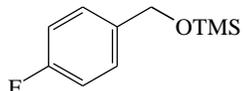
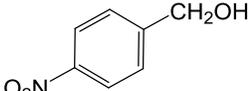
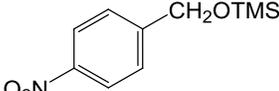
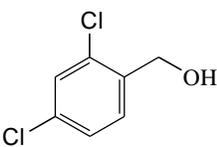
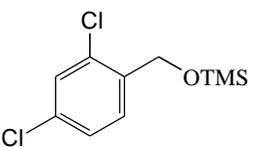
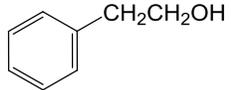
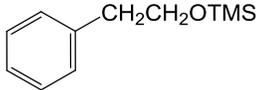
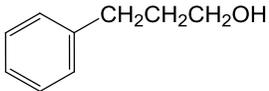
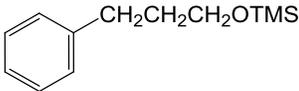
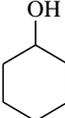
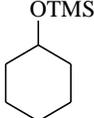
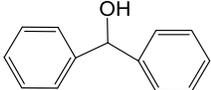
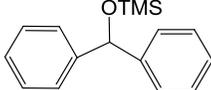
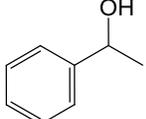
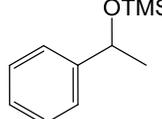
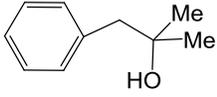
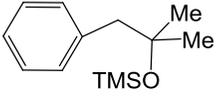
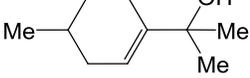
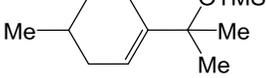
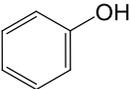
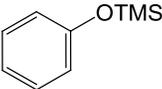
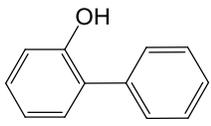
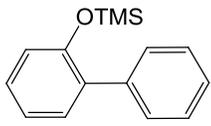
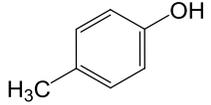
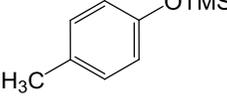
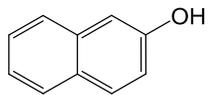
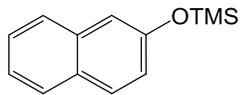
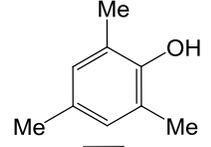
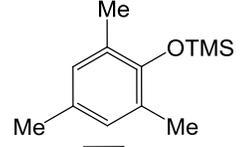
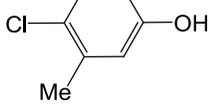
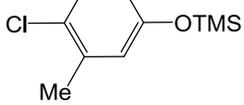
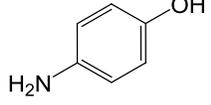
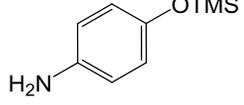
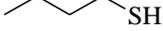
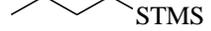
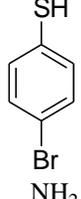
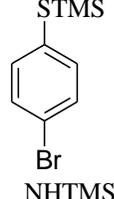
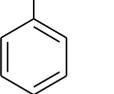
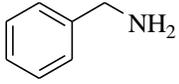
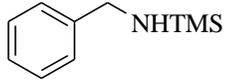
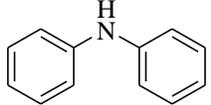
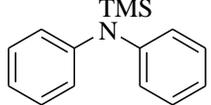
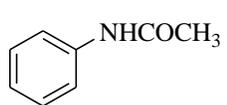
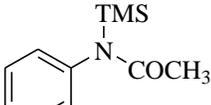
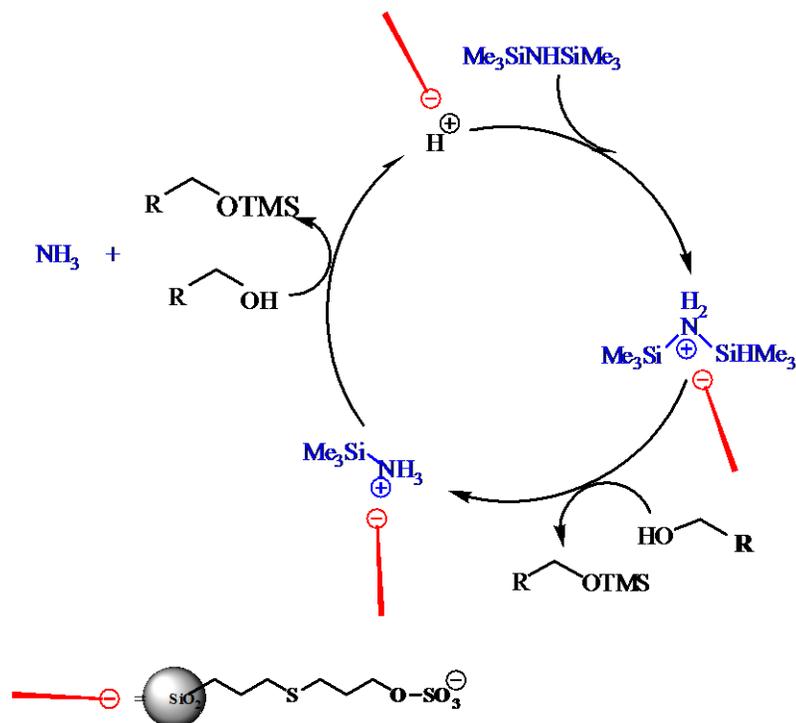
Entry	Substrate	Product	Time (min)	Yield ^a (%)
1			4	95
2			4	93
3			6	91
4			7	92
5			9	89
6			8	91
7			9	89
8			3	93
9			4	92
10			7	90
11			4	92
12			5	92
13			24h	Trace
14			24h	<30

Table 3. (Continued)

Entry	Substrate	Product	Time (min)	Yield ^a (%)
15			4	91
16			17	89
17			6	92
18			5	92
19			3	92
20			4	91
21			5	90
22			180	No Reac.
23			180	No Reac.
24			180	No Reac.
25			180	No Reac.
26			180	No Reac.
27			180	No Reac.

^aIsolated yield.



Scheme 3. Proposed mechanism for the conversion of alcohols into corresponding silyl ether in the presence of SASPSPE as cocatalyst.

Therefore, we employed the optimized conditions for the conversion of various hydroxyl groups into the corresponding silylether (Scheme 2). Next, we prepared a range of silylethers under the following reaction conditions: hydroxyl compound (1 mmol), HMDS (0.8 mmol), catalyst SASPSPE (0.015 g), and acetonitrile (2 mL) (Table 3). A wide range of alcohols underwent silylation by this procedure to provide the corresponding TMS ethers in good to excellent yields. Benzylic alcohols, phenols, and primary and secondary alcohols generally were faster than tertiaryalcohols. Trimethylsilylation of hydroxyl groups produce corresponding trimethylsilylated compounds under these conditions, whereas 1-butantiol, thiophenol (Table 3, entries 22 and 23), aniline derivatives and aliphatic amines (Table 3, entries 24-26) and *N*-phenyl acetamide (Table 3, entry 27) remained intact under the reaction conditions. It's worthy to mention that in the case of *p*-aminophenol only the phenolic group reacted under these conditions and the amino group remained intact (Table 3, entry 21). To show the efficiency of the SASPSPE in comparison with previously reported procedures in the literature, Table 4 compares some of our results with $\text{LiClO}_4\text{-SiO}_2$ [25], H- β -zeolite [23], $\text{MgBr}_2\cdot\text{OEt}_2$ [24], sulfonic acid-functionalized silica [27], tungstophosphoric acid [19], and alumina sulfuric acid [26], with respect to reaction times, yields of obtained products. It is clear from the results shown in Table 4, which silylation reactions carried out with SASPSPE required shorter reaction times and lower catalyst loading. In all reactions, fast evolution of ammonia gas was observed

(HMDS is stronger base than NH_3). It was understood by keeping a piece of turnsole paper on the top of the reaction mixture when turnsole was turned to blue color. With this observation we have proposed a mechanism in which the generation of NH_3 and catalytic role of SASPSPE in a catalytic cycle is clarified (Scheme 3). The possibility of recycling the catalyst was examined. For this purpose, the reaction of 4- bromo benzyl alcohol and HMDS was studied in acetonitrile at room temperature in the presence of SASPSPE. When the reaction was complete, the mixture was filtered and the solid was washed with dichloromethane,

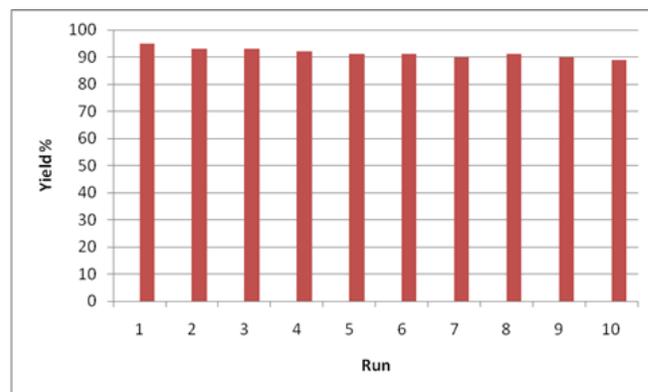
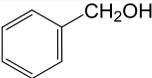
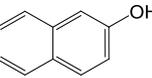
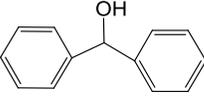
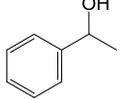
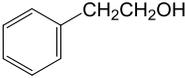


Fig. 1. Recyclability of sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl)ester in the silylation of benzyl alcohol with HMDS at room temperature. Time = 4 min.

Table 4. Comparison of the results Catalysts SASPSPE (I)^a with tungstophosphoric acid (II)^b [19], LiClO₄-SiO₂ (III)^c [25], alumina sulfuric acid (IV)^d [26], sulfonic acid-functionalized silica (V)^e [27], silica sulfuric acid (VI)^f [28], and SBSSA (VII)^g [35], in the synthesis of trimethylsilyl ether using HMDS

Entry	Substrate	Time (min)/ yield (%) ^h						
		I	II	III	IV	V	VI	VII
1		4/95	23/90	5/98	2/98	80/100 ⁱ	10/93	5/94
2		5/92	6/90	120/84	4/95	420/80 ⁱ	-	5/93
3		4/92	48/93	50/87	7/89	60/98 ⁱ	10/85	3/90
4		5/92	16/93	30/89	8/91	-	15/89	3/91
5		3/93	-	-	12/97	40/100 ⁱ	-	3/95

The equivalent ratios of substrate/ HMDS/ catalyst are ^a1/ 0.8/ 0.015 (g), ^b1/ 0.8/ 0.028 (g), ^c1/1.5/0.04 (g), ^d1/ 0.75/ 0.025 (g), ^e1/ 0.6/ 0.003, ^f1/ 0.8/ 0.08 (g), ^g1/0.8/0.015 (g) respectively. ^hIsolated Yield. ⁱGC Yield.

and recycled catalyst was saved for the next reaction. The recycled catalyst could be directly reused ten times without any treatment. No observation of appreciable loss in the catalytic activity of SASPSPE was observed (Figures 1).

4. Conclusion

In conclusion, SASPSPE has been employed for the silylation of hydroxy groups with HMDS. The attractive features of this procedure are the mild reaction conditions, high conversions, cleaner reaction profiles, reusable and environmentally friendly catalyst, all of which lead to an interesting strategy for the preparation of silyl ethers.

Acknowledgments

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