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A Facile and Efficient Trimethylsilylation of Hydroxyl Groups Using Silica-Supported Zinc Chloride and Alumina-Supported Sodium Hydrogensulfate as Recyclable Heterogeneous Catalysts

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A Facile and Efficient Trimethylsilylation of Hydroxyl Groups Using Silica-Supported Zinc Chloride and Alumina-Supported Sodium Hydrogensulfate as Recyclable Heterogeneous Catalysts

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Silica-supported zinc chloride ($\text{SiO}_2\text{-ZnCl}_2$) and novel alumina-supported sodium hydrogensulfate ($\text{NaHSO}_4\text{-Al}_2\text{O}_3$) as recyclable heterogeneous catalysts have been used for the mild trimethylsilylation of hydroxyl groups under ambient conditions. This procedure also allows for the selective protection of primary and secondary alcohols in the presence of tertiary alcohols.

Keywords Heterogeneous catalyst; $\text{NaHSO}_4\text{-Al}_2\text{O}_3$; $\text{SiO}_2\text{-ZnCl}_2$ (silzic); O-trimethylsilylation

INTRODUCTION

There is current and general interest in heterogeneous systems because of their importance in industry and in the development of new technologies.¹ Heterogeneous reagent systems have many advantages, such as simple experimental procedures, mild reaction conditions, and minimum chemical wastes, when compared to analogous liquid-phase reactions.² Solid acid catalysts 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 conditions. So far, several number

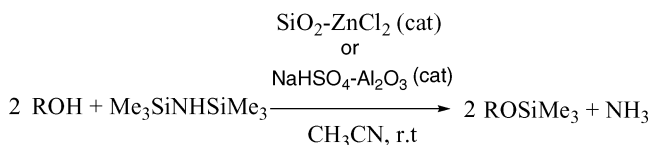
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of silica-³ and alumina-supported⁴ reactions have been reported in the literature for chemical transformations.

Hexamethyldisilazane (HMDS) is frequently used for the trimethylsilylation of hydroxyl groups. The low silylation power of HMDS is the main drawback to its application.^{5–24} We now show that SiO₂-ZnCl₂ (silzic) and NaHSO₄-Al₂O₃ as recyclable heterogeneous catalysts can be used to activate this reagent at room temperature (Scheme 1).



R = aryl, primary, secondary, tertiary alcohol and oxime

SCHEME 1

These heterogeneous catalysts are safe, inexpensive, recyclable, easy to handle, environmentally benign, present fewer disposal problems, and stable in reaction media.

RESULTS AND DISCUSSION

Silzic was prepared according to the reported procedure, and was characterized by comparison of XRD, TGA, DSC, and BET with authentic sample.²⁵ NaHSO₄-Al₂O₃ was reported for the first time. The idea for synthesis of alumina-supported sodium hydrogensulfate (NaHSO₄-Al₂O₃) is based on the preparation of silica-supported sodium hydrogensulfate, which was first synthesized by Breton.²⁶

To optimize the reaction conditions, initially we converted benzyl alcohol (1 mmol) to its corresponding benzyl trimethylsilyl ether with the amount of SiO₂-ZnCl₂ (0.025 g) as catalyst and HMDS (0.75 mmol) in the presence of various solvents and also solvent-free conditions at room temperature (Table I). The results in Table I show that among these solvents, acetonitrile was the solvent of choice in terms of time.

To find out the optimum quantity of the catalyst, the reaction of benzyl alcohol (1 mmol) with HMDS (0.75 mmol) was carried out using different quantities of SiO₂-ZnCl₂ under ambient conditions in acetonitrile as solvent (Table II). As can be seen from Table II, the best results were obtained using 0.025 g of the catalyst.

This reaction was also performed to optimize the organic solvent (THF, CH₂Cl₂, MeCN, EtOAc, n-hexane, CHCl₃, diethyl ether) or solvent-free, and also the amount of the NaHSO₄-Al₂O₃ as catalyst

TABLE I Preparation of Benzyl Trimethylsilyl Ether Using SiO₂-ZnCl₂ (0.025 g) as Catalyst Under Solvent and Solvent-Free Conditions at Room Temperature

Entry	Solvent	Time (min)	GC yield (%)	Yield (%) ^a
1	Dichloromethane	365	100	87
2	Chloroform	660	100	85
3	Ethyl acetate	425	100	81
4	n-Hexane	360	100	89
5	Acetonitrile	5	100	93
6	Solvent-free	95	100	87

^aIsolated yield and the product gave satisfactory IR and NMR spectra.

(0.0125, 0.025, 0.05 g). The best results were obtained using 0.05 g of the catalyst in acetonitrile (2 mL) as solvent.

Thus, we prepared a range of silylethers under the optimized reaction conditions: hydroxyl compound (1 eq), HMDS (0.75 eq), SiO₂-ZnCl₂ (0.025 g) or NaHSO₄-Al₂O₃ (0.05 g) as catalysts, and acetonitrile (2 mL) (Table II).

A wide range of structurally diverse and functionalized phenols, alcohols, and oximes underwent silylation by this procedure to provide the corresponding TMS ethers in good to excellent isolated yields (Table III). Primary alcohols mostly reacted faster than secondary and tertiary alcohols. Generally, in the all cases of benzyl, primary, secondary, and tertiary alcohols, the reactions were completed within less than 25 min at ambient conditions accompanied by evolution of NH₃ gas from the reaction mixture. The amine functional group in 4-aminophenol (Table III, Entry 23) remained unaffected under the reaction conditions. In order to examine the functional group compatibility, we test some more alcohols having other functional groups such as carbonyl group, amino group, alkene, and ethers. Alcohols were successfully converted to the corresponding silyl ethers, whereas, other functional groups were intact (Table III, Entries 2, 5, 23, and 24).

TABLE II Optimization Amount of SiO₂-ZnCl₂ Catalyst in the Synthesis of Benzyl Trimethylsilyl Ether

Entry	Catalyst (g)	Time (min)	Isolated yield (%)
1	0.05	3	87
2	0.025	5	93
3	0.01	17	90

TABLE III Silylation of Alcohols, Phenols, Naphthols, and Oximes with HMDS in the Presence of SiO₂-ZnCl₂ (0.025 g) and NaHSO₄-Al₂O₃ (0.05 g) as Catalysts in Acetonitrile as Solvent

Entry	Substrate	SiO ₂ -ZnCl ₂		NaHSO ₄ -Al ₂ O ₃	
		Time (min)	Yield (%) ^a	Time (min)	Yield (%) ^a
1	Benzyl alcohol	5	93–95 ^b	2	95–97 ^b
2	4-Methoxybenzyl alcohol	8	93	6	94
3	2-Phenyl ethanol	11	96	13	95
4	Diphenyl methanol	13	95	6	94
5	Allyl alcohol	12	82	7	90
6	1-Butanol	8	81	5	85
7	3-Methyl-1-butanol	10	83	6	87
8	Cyclohexanol	16	95	9	92
9	<i>tert</i> -Butanol	17	85	15	90
10	Tetrahydro-2-furylmethanol	13	93	8	90
11	5-Methyl-2-(1-ethylmethyl) cyclohexanol	15	96	15	95
12	1,4-Butandiol	10	87 ^c	8	90 ^c
13	Tricyclo[3,3,1,1 ^{3,7}] doc-1-ol	21	98	16	97
14	1-Octanol	11	96	10	95
15	2-Octanol	25	94	12	94
16	Phenol	7	96	4	96
17	4-Methylphenol	8	96	5	93
18	3-Methylphenol	10	89	6	90
19	2-Methylphenol	12	85	8	90
20	1-Naphthol	20	97	15	98
21	2-Naphthol	17	96	14	94
22	Benzaldehyde oxime	8	91	9	90
23	4-Aminophenol	9	90	6	87
24	Benzoin	25	81	4	80

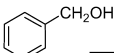
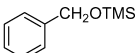
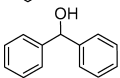
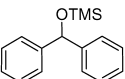
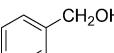
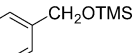
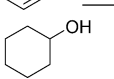
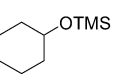
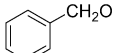
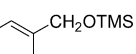
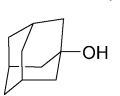
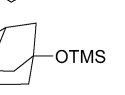
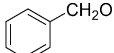
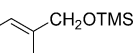
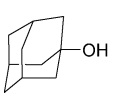
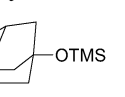
^aThe pure isolated products were characterized by the comparison of their physical data with those of known compounds.^{5–24}

^bIsolated yields after five times recovery of the catalyst.

^cThe amount of HMDS was chosen (1.5 mmol).

We also investigated selective silylation of different binary mixtures of alcohols (Table IV). This method was shown to be highly selective for primary alcohols, such as benzyl alcohols, compared to secondary and tertiary alcohols (Table III, Entries 1–4). The primary alcohols were completely converted to the corresponding silylether, while the secondary and tertiary alcohols were converted to the corresponding silylated product with 2–10% yield in the presence of SiO₂-ZnCl₂ and NaHSO₄-Al₂O₃ as catalyst.

TABLE IV Selective Silylation of Different Binary Mixtures of Alcohols

Entry	Binary mixture		Molar Ratio Substrate 1/ Substrate 2 /HMDS/Catalyst (g)	Time (min)	GC yield (%)
	Substrate	Product			
1			1/1/0.75/0.025 ^a	10	100
					10
2			1/1/0.75/0.025 ^a	10	100
					10
3			1/1/0.75/0.025 ^a	10	100
					5
4			1/1/0.75/0.05 ^b	10	100
					2

^aCatalyst: SiO₂-ZnCl₂.^bCatalyst: NaHSO₄-Al₂O₃.

The reusability of the catalysts is an important benefit and makes them useful for commercial applications. Thus, the recovery and reusability of SiO₂-ZnCl₂ and NaHSO₄-Al₂O₃ were investigated. The recyclability of the catalyst in the reaction of benzyl alcohol and HMDS in the presence of these catalysts was checked (Table III, Entry 1). The separated catalyst can be reused after washing with n-hexane and drying at 100°C. The catalyst was recovered in excellent yields; after it was used in the mentioned reaction five times, it showed the same activity as fresh catalyst without any loss of its activity.

EXPERIMENTAL

All reagents were purchased from Merck and Aldrich and used without further purification. SiO₂-ZnCl₂ was prepared according to the

reported procedure.²⁵ All yields refer to isolated products after purification. Products were characterized by comparison with authentic samples and by spectroscopy data (IR, ¹H NMR spectra). The NMR spectra were recorded on a Bruker Avance DPX 300 and 500 MHz instrument. The spectra were measured in CDCl₃ relative to TMS (0.00 ppm). GC analysis was run with Shimadzu GC-14A. IR spectra were recorded on a JASCO FT-IR 460plus spectrophotometer. TLC was performed on silica-gel polygram SIL G/UV 254 plates.

Preparation of Alumina-Supported Sodium Hydrogensulfate (NaHSO₄-Al₂O₃)

NaHSO₄-Al₂O₃ was reported for the first time. The idea for synthesis of alumina-supported sodium hydrogensulfate (NaHSO₄-Al₂O₃) is based on the preparation of silica-supported sodium hydrogensulfate, as it was first synthesized by Breton,²⁶ by the following procedure.

To a solution of 4.14 g (0.03 mol) of NaHSO₄·H₂O in 20 mL of water in a 100-mL beaker containing a stir bar, 10 g of Al₂O₃ was added. The mixture was stirred for 15 min and then gently heated on a hot plate, with intermittent swirling, until a free-flowing white solid was obtained. The catalyst was further dried by placing the beaker in an oven maintained at 120°C for at least 48 h prior to use.

The amount of H⁺ in the NaHSO₄-Al₂O₃ was determined by acid-base titration according to the following reaction (Equation 1):



The librated H₃O⁺ was titrated by standard NaOH, and the amount of H⁺ in NaHSO₄-Al₂O₃ was calculated (1 g of NaHSO₄-Al₂O₃ equal to 0.085 mmol H⁺).

X-Ray Diffraction (XRD) of NaHSO₄-Al₂O₃

Powder X-ray diffraction (XRD) measurements were performed using D8 Advance diffract meter made by a Bruker AXS company in Germany. Scans were taken with a 2θ step size of 0.02 and a counting time of 1.0s using a CuK_α radiation source generated at 40 KV and 30 mA. Specimens for XRD were prepared by compaction into a glass-backed aluminum sample holder. Data was collected over a 2θ range from 4° to 70°, and phases were identified by matching experimental patterns to entries in the Diffra^{plus} version 6.0 indexing software. The catalyst containing alumina-supported sodium hydrogensulfate was characterized by XRD, and the pattern is presented in Figure 1. As is shown in

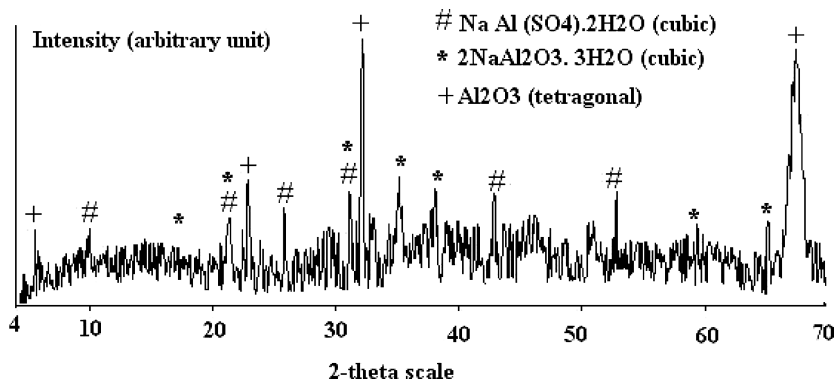


FIGURE 1 XRD pattern of alumina-supported sodium hydrogensulfate.

this figure, the actual phases that were identified for this catalyst under the specified preparation conditions were $\text{NaAl}(\text{SO}_4) \cdot 2\text{H}_2\text{O}$ (cubic), $2\text{NaAl}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (cubic), and Al_2O_3 (tetragonal), and it is considered that the high catalyst performance for this catalyst is attributed to these phases.

Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) of $\text{NaHSO}_4\text{-Al}_2\text{O}_3$

The weight change of the catalyst was measured using a TGA/DSC simultaneous thermal analyzer apparatus from Rheometric Scientific Company (STA 1500+ Model) under a flow of dry air. The temperature was raised from room temperature to 500°C using a linear programmer at a heating rate of 5°C per min. The TGA and DSC curves for the catalyst are illustrated in Figure 2. The weight losses found from TGA measurements agree fairly well with those expected for the decomposition of alumina-supported sodium hydrogensulfate to alumina and Na_2SO_4 and other stable phases. For the this catalyst, the thermogravimetric curve seems to indicate tree-stage decomposition, which is considered to be due to the removal of physical absorbed water and crystalline water ($70\text{--}140^\circ\text{C}$), and the second stage is due to the decomposition of sodium hydrogensulfate ($150\text{--}230^\circ\text{C}$), respectively. The peak around $280\text{--}350^\circ\text{C}$ is due to the decomposition of sodium hydrogensulfate to sulfate and sodium sulfate. The TGA curve is involved with a total overall weight loss of ca. 23 wt%. DSC measurement was performed in order to provide further evidence for the presence of the various species and evaluates their thermal behavior. As shown in Figure 2, the endothermic peak at lower temperature represents the removal

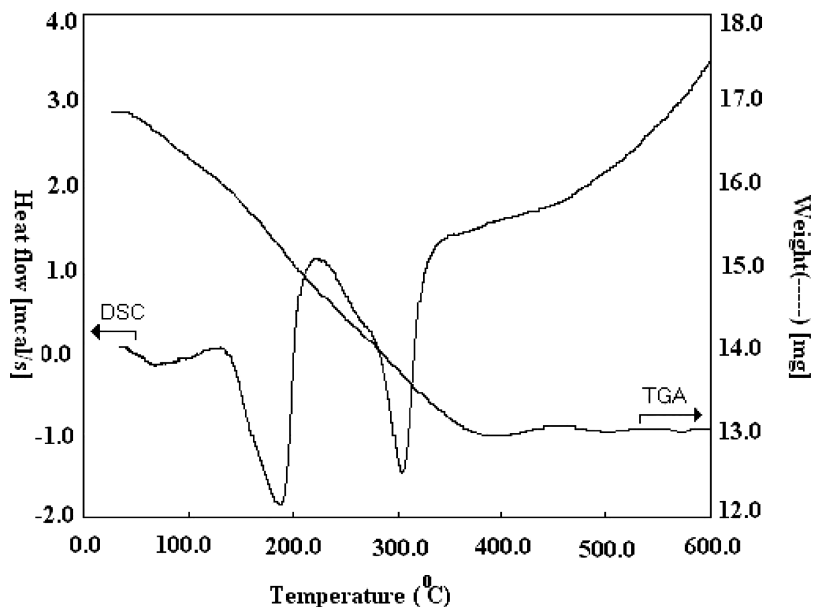


FIGURE 2 Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) of alumina-supported sodium hydrogensulfate.

of the physically adsorbed water and crystalline water from the material, while the endothermic peak at higher temperature represents solely the decomposition of the sodium hydrogensulfate to sulfate and sodium sulfate.

Specific Surface Area, Total Pore Volume, and Average Pore Diameter of $\text{NaHSO}_4\text{-Al}_2\text{O}_3$

N_2 adsorption measurements of the catalyst were carried out using micrometrics adsorption equipment (Quantachrome instrument, model Nova 2000, USA). N_2 (99.99%) as the analysis gas and the catalyst samples were slowly heated to 120°C for 3 h under nitrogen atmospheric. The specific surface area measurements were evacuated by BET, BJH, and DH methods and also total pore volume and average pore diameter were calculated from the nitrogen adsorption/desorption curve using the BJH and DH methods at -196°C for 300 minutes. Characterization of the catalyst was carried out using N_2 adsorption/desorption measurements, and the results are given in Table V. These results show that the catalyst have high specific surface area and high pore volume, and this

TABLE V Specific Surface Area, Total Pore Volume, and Average Pore Diameter of Pure Alumina and Alumina-Supported Sodium Hydrogensulfate

Sample	Specific surface area (m ² /g)			Pore diameter (Å)		Pore volume (× 10 ² cc/g)	
	BET	BJH	DH	BJH	DH	BJH	DH
Al ₂ O ₃	182.3	181.1	179.9	17.12	17.12	9.03	8.98
NaHSO ₄ -Al ₂ O ₃	167.7	169.3	170.8	18.77	18.77	8.32	8.01

is the reason for the high catalytic performance of alumina-supported sodium hydrogensulfate in the experimental conditions.

General Procedure for Trimethylsilylation of Hydroxyl Compounds Using SiO₂-ZnCl₂ and NaHSO₄-Al₂O₃ as Catalyst

To a stirred solution of alcohols or oximes (1 mmol), HMDS (0.75 mmol) and acetonitrile as solvent (2 mL), and SiO₂-ZnCl₂ (0.025 g) or NaHSO₄-Al₂O₃ (0.05 g) were added at room temperature, and the mixture was stirred for the appropriate time (Table III). The reaction was followed by TLC (n-hexane–EtOAc, 9:1). After completion of the reaction, the catalyst was filtered. The resulting mixture was passed through a short pad of silica gel. Then, the pad column was washed with n-hexane (2 × 10 mL). Evaporation of the solvent under reduced pressure gave pure product(s) (Table III). The desired pure products were characterized by comparison of their physical data with those of known compounds.^{5–24}

CONCLUSION

In summary, SiO₂-ZnCl₂ and NaHSO₄-Al₂O₃ are effective catalysts for O-trimethylsilylation of primary and secondary unhindered alcohols, and also for secondary hindered and tertiary ones, oximes and phenols. These excellent heterogeneous catalysts allow the reactions to be performed in ambient conditions with good to excellent yields. The degree of selectivity of primary over secondary and tertiary is good to excellent. NaHSO₄-Al₂O₃ was reported and characterized for the first time. Simple work-up procedure and reusability of these catalysts are other advantages of these methods.

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