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ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

DOI: 10.1039/C4RA04911J

Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Tributyltin Grafted onto the Surface of 3-Aminopropyl Functionalized γ- Fe_2O_3 Nanoparticles: A Magnetically-recoverable Catalyst for Trimethylsilylation of Alcohols and Phenols

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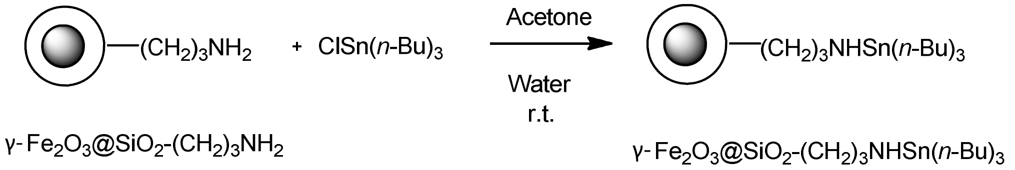
Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Bonding of a homogenous tributyltin chloride catalyst on the surface of functionalized magnetic nanoparticles provides a new stable, efficient and magnetically recyclable catalyst for trimethylsilylation of alcohols and phenols with hexamethyldisilazan under mild reaction conditions. The catalyst showed good stability and could be reused at least 10 times. The catalyst was characterized using spectroscopic, magnetic, and thermal techniques (FT-IR, SEM, TEM, XRD, ICP, VSM, and TGA).

Today, much attention is given to designing strategies for fully recoverable heterogeneous metal catalysts enabling recovery and disposal at low costs,[1] although a majority of chemical transformations are catalyzed by homogenous transition metal catalysts. The application of magnetic-supported catalysts is a possible solution for this in which the catalyst is separated using an external magnetic field. Such catalysts could have longer lives, minimizing the change in activity and selectivity over homogeneous catalysts.[2-5] Magnetic nanoparticles coated with a layer of silica chains with a covalently functionalized organic layer have drawn attention, because the functionalized layer allows chemical and biological modification on the surface of the silica layer.[6] In this type of solid catalyst, the flexibility of the catalytic centers are similar to those of their homogeneous counterparts with the advantage of thermal stability of the support and magnetic recyclability of the magnetic cores. Homogenous tin catalysts have been extensively used as stoichiometric catalysts or reagents for organic transformation;[7-10] however, the hygroscopic nature of these compounds and their solubility in organic solvents hampers their use as reusable catalysts or reagents in organic reactions. Tin species have been grafted onto several organic, inorganic and polymeric supports to stabilize active sites and to facilitate recovery as catalysts for organic transformation.[11-14] Leaching of the metal from the support during the reaction is a serious drawback to these types of heterogeneous catalysts; therefore, covalent bonding of the catalyst to an insoluble support is of practical importance. This paper describes the preparation of maghemite nanoparticles coated with amino-functionalized silica attached to a tributyltin catalyst (γ-Fe_2O_3@SiO_2-$(CH_2)_3$NH-Sn(*n*-Bu)$_3$), (Scheme 1). In this material, tributyltin species is chemically bonded to the support, which prevents leaching of the metal during the reaction and therefore, represents an improvement over existing methods.

Silylation of alcohols is an organic transformation of great interest because of their importance in the synthesis of fine chemicals and natural products.[15-16] Substitution of hydrogen atom of a hydroxyl group with a trimethysilyl group results in decreased polarity and increased solubility in organic solvents and increased thermal stability and volatility for GC-MS analysis.[17] Hexamethyldisilazane (HMDS) is the most popular silylating agent because it is stable, commercially available, inexpensive, and it only produces NH_3 as a reaction by-product which can leave the reaction mixture driving the reaction to completion.[18] The only disadvantage of HMDS is its low reactivity, which requires activation. Different methods have been reported for the activation of HMDS. Excellent yields have been obtained for some cases,[14, 19-21] however, in some procedures, there are disadvantages such as long reaction times,[22] tedious work-up and, poor recyclability of the catalyst.[23-25]

The present study reports on the catalytic application of tributyltin-supported amino-functionalized silica-coated magnetic nanoparticlesas, a magnetically separable catalyst for the activation of HMDS for protection of different hydroxyl groups at room temperature.



Scheme 1 Synthesis of tributyltin catalyst bonded to the surface of 3-aminopropyl-functionalized γ-Fe_2O_3 nanoparticles

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DOI: 10.1039/C4RA04911J

Cite this: DOI: 10.1039/c0xx00000x

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In this research, 3-aminopropyl-functionalized silica-coated maghemite nanoparticles (γ-Fe_2O_3@SiO_2-$(CH_2)_3NH_2$) were synthesized as reported by the reaction of silica-coated maghemite nanoparticles (γ-Fe_2O_3@SiO_2) and 3-aminopropyltrimethoxysilane.[26-27] Aminopropyl-functionalized silica-coated magnetic nanoparticles are ideal supports because the amino groups can easily be used for surface modification by nucleophilic substitution.[27-28]

The FT-IR spectrum of the γ-Fe_2O_3@SiO_2-$(CH_2)_3NH_2$ nanoparticles is shown in Fig. 1. The broad absorption band at 3437 cm^{-1} was assigned to surface hydroxyl groups and the strong bands at 1094 cm^{-1} (ν_{as}(Si–O–Si)) and 802 cm^{-1} (ν_s(Si–O–Si)) are in good agreement with the IR results reported in the literature.[28] The outer shell of the amino-functionalized silica provided suitable sites ($-NH_2$ groups) for surface functionalization with the tin catalyst.

The γ-Fe_2O_3@SiO_2-$(CH_2)_3NH_2$ organic–inorganic hybrid material was affected by an acetone-water solution of tributyltin chloride at room temperature. After 24 h, the brown powder was washed with deionized water and ethanol and then dried at 100 °C for 12 h, leading to formation of covalently immobilized tributyltin supported on magnetic nanoparticles; γ-Fe_2O_3@SiO_2-$(CH_2)_3NH$-$Sn(n\text{-}Bu)_3$.

Immobilization of tributyltin moiety onto the surface of the aminopropyl-functionalized γ-Fe_2O_3@SiO_2 magnetic nanoparticles was confirmed by FT-IR, which showed characteristic CH_2 stretching vibration bands of butyl groups at 2927 cm^{-1} and 2858 cm^{-1},[29] 1367 cm^{-1} (C-H bending of butyl groups),[30] 1093 cm^{-1} (asymmetric stretching of Si–O–Si), 803 cm^{-1} (symmetric stretching of Si–O–Si or a stretching vibration of Fe–O bonds), 567 cm^{-1} (vibration of γ-Fe–O), and 463 cm^{-1} (bending modes of Si–O–Si).[27] The FT-IR spectra of γ-Fe_2O_3@SiO_2-$(CH_2)_3NH_2$, γ-Fe_2O_3@SiO_2-$(CH_2)_3NH$-$Sn(n\text{-}Bu)_3$ and tributyltin chloride samples are shown in Fig. 1.

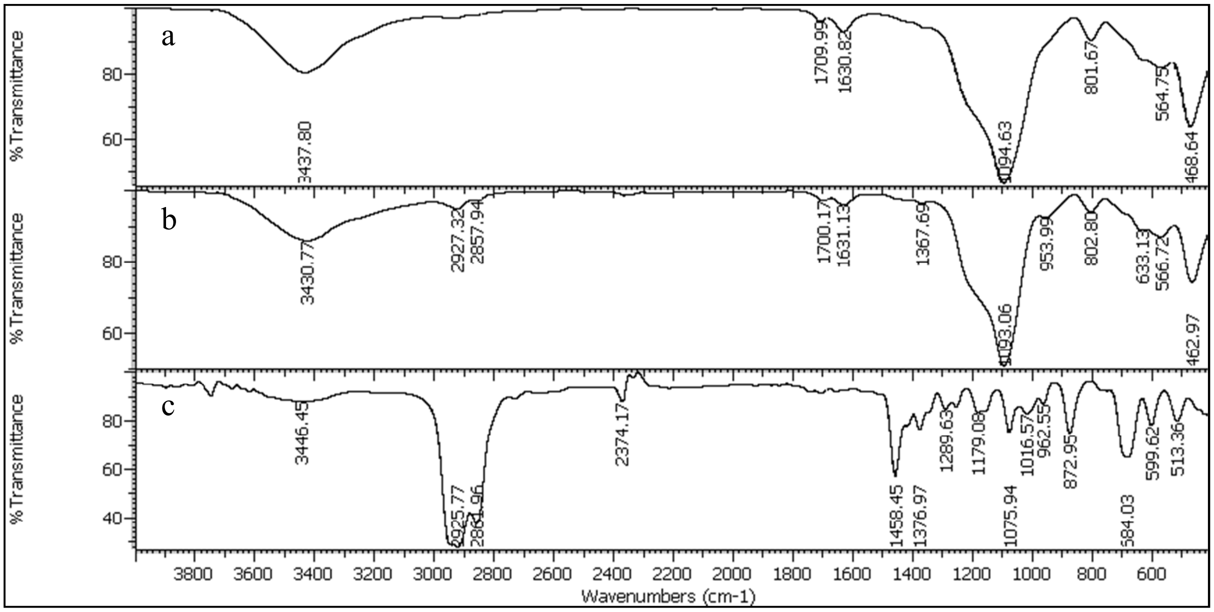

Figure 1 FT-IR spectra of (a) γ-Fe_2O_3@SiO_2-$(CH_2)_3NH_2$, (b) γ-Fe_2O_3@SiO_2-$(CH_2)_3NH$-$Sn(n\text{-}Bu)_3$ and (c) tributyltin chloride

The characteristic bands were at the same wave numbers with small shifts according to the interaction with the support. Fig. 2, (a) and (b) shows the SEM and TEM images for the γ-Fe_2O_3@SiO_2-$(CH_2)_3NH$-$Sn(n\text{-}Bu)_3$. The TEM images of the catalyst (γ-Fe_2O_3@SiO_2-$(CH_2)_3NH$-$Sn(n\text{-}Bu)_3$ were taken using a 80 kV Zeiss-EM10C instrument and shows the core-shell structure of the particles (Fig. 2, (b)). On the other hand, this image confirms that the particles are nanosized.

The XRD pattern of the catalyst showed diffraction peaks at around 17.00°, 21.27°, 35.29°, 41.62°, 50.73°, 63.48°, 67.63° and, 74.66° corresponding to the (110), (111), (220), (311), (400), (422), (511) and, (440), respectively. These diffraction peaks are in good agreement with the tetragonal structure of the γ-Fe_2O_3 (Fig. 2, (c)).[27]

Thermo-gravimetric analysis (TGA) was recorded by heating the sample at a rate of 10 °C min^{-1}, and indicated that the material was stable up to 300 °C (Fig. 2, (d)). The 7% weight loss at ~300-490 °C can be attributed to decomposition of organic functionalities. Major weight loss at high temperatures is characteristic of chemisorbed materials and confirms that the aminopropyl group is chemically bound to the surface of the silica.[28] The amount of the metal supported onto the γ-Fe_2O_3@SiO_2-$(CH_2)_3NH_2$ was determined by induced coupled plasma (ICP) analysis and was 0.0049 g of Sn per g of catalyst (0.041 mmol g^{-1}).

The hysteresis loop were measured for the γ-Fe_2O_3@SiO_2-

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$(CH_2)_3NH$-$Sn(n$-$Bu)_3$ in an applied magnetic field at ambient temperatures with the field sweeping from −8000 to +8000 Oersted. As shown in Fig. 2(e). The M (H) hysteresis loop was completely reversible, indicating that the nanoparticles exhibited super-paramagnetic characteristics. Saturation magnetization (M_s) for γ-Fe_2O_3@SiO_2-$(CH_2)_3NH$-$Sn(n$-$Bu)_3$ was 14.48 emu.g^{-1}, demonstrating that the nanoparticles exhibit high permeability in magnetization, which was sufficient for magnetic separation using a conventional magnet.

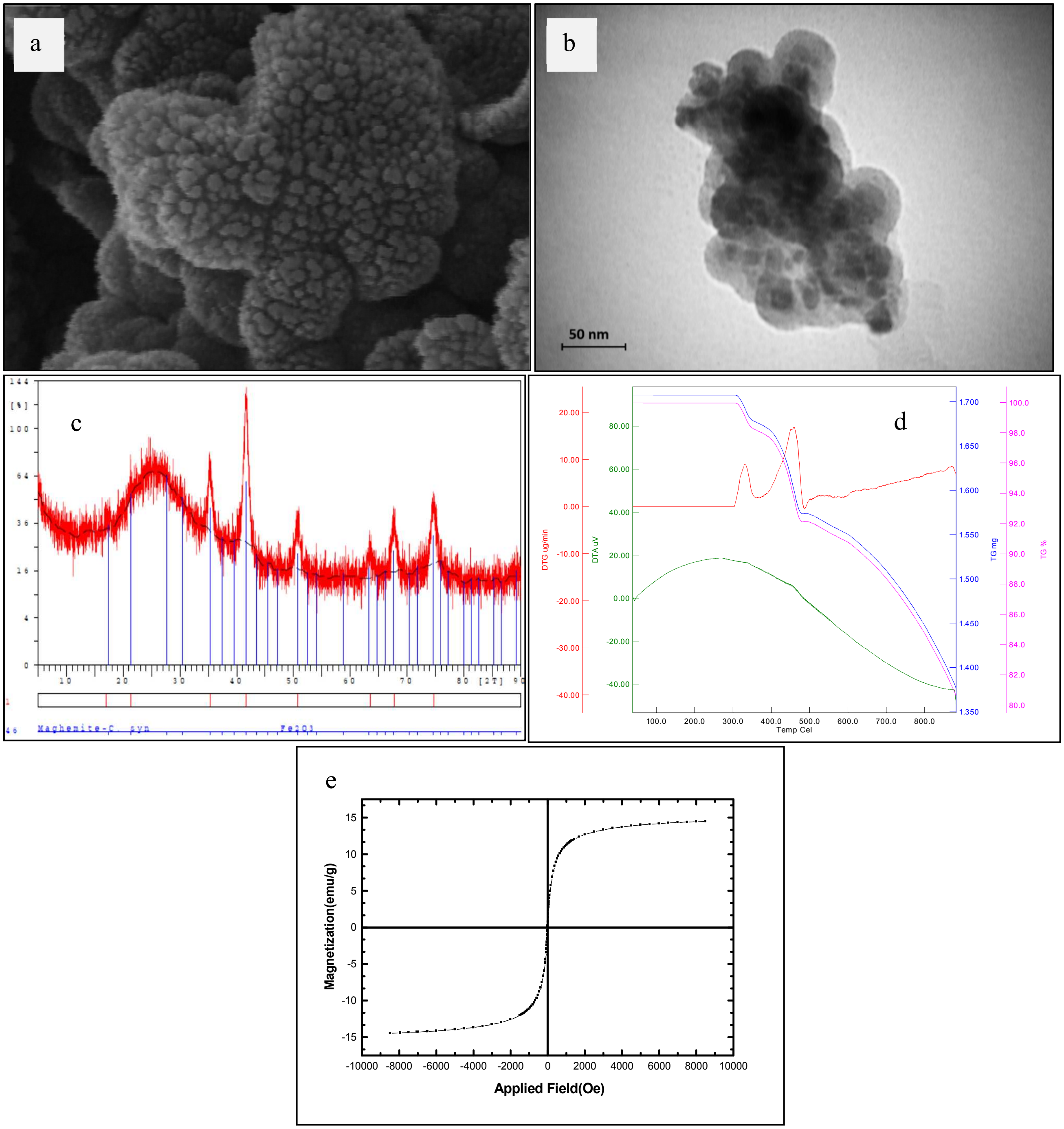

Figure 2 a) SEM image, b) TEM image, c) XRD spectrum, d) TGA diagram, and e) Vibrating Sample Magnetometer (VSM) curve of the γ-Fe_2O_3@SiO_2-$(CH_2)_3NH$-$Sn(n$-$Bu)_3$

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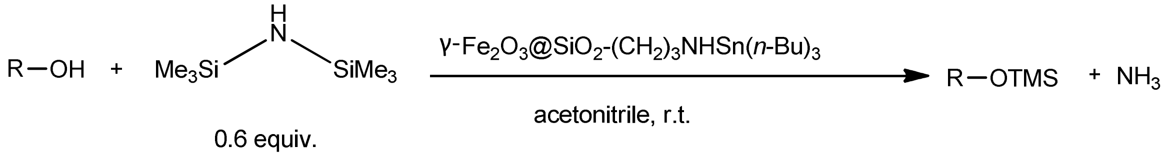

Scheme 2 Synthesis of trimethylsilyl ethers with HMDS in the presence of γ-$Fe_2O_3@SiO_2$-$(CH_2)_3$NH-Sn(n-Bu)$_3$

The catalytic activity of the prepared catalyst was tested for the trimethysilylation of alcohols and phenols with HMDS under mild reaction conditions (Scheme 2). To optimize the reaction conditions, the silylation reaction of benzyl alcohol with HMDS was investigated in the presence of different catalysts. The silylating power of HMDS can be increased by different (mostly acidic) catalysts.[18] Silica-coated magnetic nanoparticles (γ-$Fe_2O_3@SiO_2$) led to 80% isolated yield of trimethylsilylbenzyl ether in 8 min (Table 1, entry 2). The reaction did not proceed using acetonitrile in the presence of basic γ-$Fe_2O_3@SiO_2$-$(CH_2)_3NH_2$ even after 24 h (Table 1, entry 3).

Tributyltin-supported aminopropyl-functionalized maghemite nanoparticles γ-$Fe_2O_3@SiO_2$-$(CH_2)_3$NH-Sn(n-Bu)$_3$ and their homogeneous analogues (tributyltin chloride) were evaluated in the trimethylsilylation of benzyl alcohol at 0.5 molar equivalents of HMDS per mole of substrate in acetonitrile to identify the catalytic activity of tributyltin supported on magnetic nanoparticles (Table 1). Catalytic amounts of tributyltin chloride (0.00041 mmol, the same amount of Sn on 10 mg of γ-$Fe_2O_3@SiO_2$-$(CH_2)_3$NH-Sn(n-Bu)$_3$), led to fast and complete conversion of benzyl alcohol to silyl ether, but recovery of the catalyst from the product was difficult because of the solubility of tributyltin chloride in conventional organic solvents (Table 1, entry 5). Trimethysilylation of benzyl alcohol with HMDS in the presence of 10 mg of the γ-$Fe_2O_3@SiO_2$-$(CH_2)_3$NH-Sn(n-Bu)$_3$ in acetonitrile led to a 90% isolated yield of trimethylsilylbenzyl ether in 3 min (Table 1, entry 4). A slight excess (0.6 equiv.) of HMDS proved to be essential for complete conversion of benzyl alcohol (Table 1, entries 4 and 6). A greater excess of HMDS (0.8 equiv.) led to no considerable change in reaction time. Different solvents were tested and acetonitrile was chosen as the best solvent for time and product yield (Table 1, entries 7-9). The optimized ratio of substrate/HMDS/catalyst was 1 mmol/ 0.6 mmol /10 mg (Table 1, entry 6). The turnover number of the catalyst was 2400,000.

Table 1 Optimization of the reaction condition for trimethysilylation of benzyl alcohol with HMDS[a]

Entry	Catalyst	HMDS (equiv.)	Solvent	Time (min.)	Yield (%)[b]
1	No catalyst	0.5	Acetonitrile	360	75
2	γ-$Fe_2O_3@SiO_2$	0.5	Acetonitrile	8	80
3	γ-$Fe_2O_3@SiO_2$-$(CH_2)_3NH_2$	0.5	Acetonitrile	360[c]	n.r.
4	γ-$Fe_2O_3@SiO_2(CH_2)_3NH_2$-Sn($n$-Bu)$_3$	0.5	Acetonitrile	3	90
5	Homogeneous tributyltin chloride[d]	0.5	Acetonitrile	0.5	95
6	γ-$Fe_2O_3@SiO_2(CH_2)_3NH_2$-Sn($n$-Bu)$_3$	0.6	Acetonitrile	3	95
7	γ-$Fe_2O_3@SiO_2(CH_2)_3NH_2$-Sn($n$-Bu)$_3$	0.6	No solvent	120	10
8	γ-$Fe_2O_3@SiO_2(CH_2)_3NH_2$-Sn($n$-Bu)$_3$	0.6	n-Hexane	120	5
9	γ-$Fe_2O_3@SiO_2(CH_2)_3NH_2$-Sn($n$-Bu$_{)3}$	0.6	Dichloromethane	120	10

[a] Reaction conditions: Benzyl alcohol (1 mmol), catalyst (10 mg), HMDS, Solvent (1 mL), r.t.

[b] Isolated yields

[c] Reaction continued even for 24 h and conversion was 0 %

[d] The reaction conducted with 0.00041 mmmol of tributyltin chloride (the same amount of Sn on 10 mg of the γ-$Fe_2O_3@SiO_2(CH_2)_3NH_2$-Sn($n$-Bu)$_3$)

The optimized condition was applied to various alcohols and phenols and the desired silyl ethers were obtained with excellent isolated yields in short reaction times. The results for the trimethysilylation of alcohols and phenols are shown in Table 2. Benzylic and primary alcohols and phenols, were generally faster than secondary and tertiary alcohols (Table 2, entries 1-10). Hydroxyl group was selectively silylated in the presence of amino or thiol groups (Table 2, entries 11-13). Aniline, benzyl amine and benzothiol remained unaffected under the reaction conditions (Table 2, entries 14-16).

A variety of aliphatic and aromatic alcohols were efficiently converted to their corresponding silyl ethers (Table 2). The reaction was operationally simple and performed with catalytic amounts of tributyltin supported on magnetic nanoparticles (0.041 mmol g^{-1}) in acetonitrile at room temperature.

Reusability of the catalyst was tested by studying the trimethysilylation of benzyl alcohol with HMDS as a model reaction under the optimized reaction conditions. The recovered catalyst was reused for 10 subsequent runs without significant loss in catalytic activity (Table 3). The filtrates of each cycle were collected for determination of Sn leaching by ICP analysis. No detectable leaching of Sn from the support was observed after ten consecutive reaction cycles (Table 3).

To check the heterogeneity of the catalyst, the supernatant of the reaction media was tested 10 min after the beginning of the reaction; the catalyst was separated using an external magnet, after which no Sn was observed in the filtrate using ICP analysis.

The evolution of gaseous ammonia (NH_3) was observed in all reactions. A plausible mechanism confirming the catalytic role of this catalyst has been proposed (Scheme 3).

A Lewis acid–base interaction between the catalyst and HMDS

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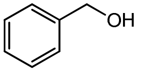
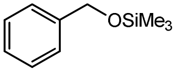
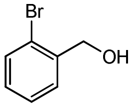
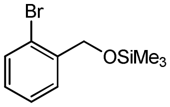
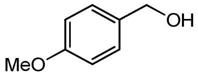
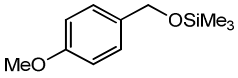
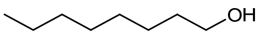
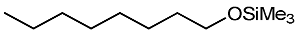
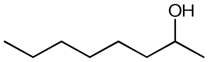
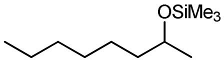
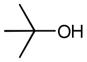
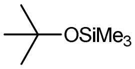
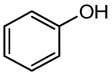
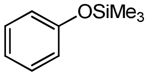
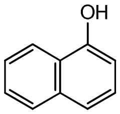
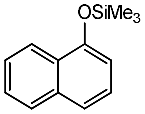
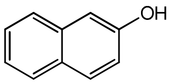
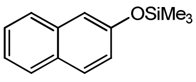
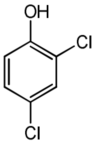
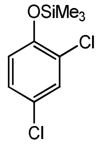
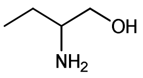
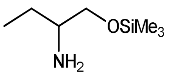
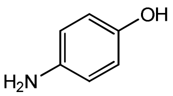
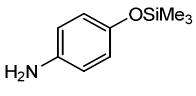
was suggested. This interaction polarized the nitrogen-silicium bond and activated the HMDS (Scheme 3). The activated organosilane (I) reacted with alcohol, giving rise to trimethyisilylated alcohol and reactive species (II). The reaction of a second equivalent of alcohol with this intermediate led to trimethysilylation of the hydroxyl group simultaneously with the release of the intermediate (III), which lost NH_3 and re-entered the catalytic cycle (Scheme 3).

Table 2 Trimethysilylation of alcohols and phenols in the presence of magnetic γ-Fe_2O_3@SiO_2-$(CH_2)_3$-NH-Sn(*n*-Bu)$_3$[a]

Entry	Substrate	Product	Time (min.)	Yield (%)[b,c]
1			3	95 (90)[d]
2			5	98
3			3	93
4			10	90
5			12	80
6			15	45
7			10	90
8			10	98
9			10	95
10			10	92
11			10	85
12			10	98

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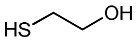
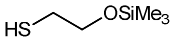
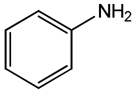
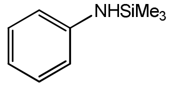
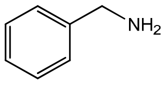
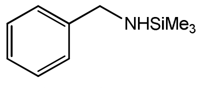
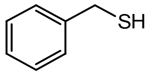
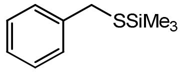
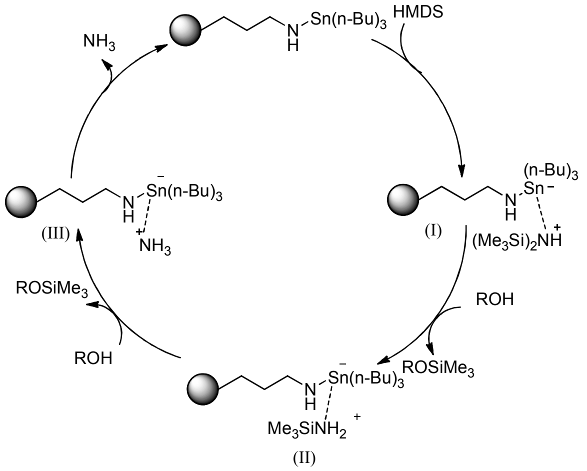
13			10	95
14			360	0
15			360	0
16			360	0

[a] Reaction conditions: substrate (1 mmol), catalyst (10 mg), HMDS (0.6 equiv.), CH_3CN (1 mL), r.t.; [b] Isolated yields.; [c] Products was confirmed comparing their physical and spectral data with those of authentic samples reported in literature.; [d] The reaction was accomplished with recycled catalyst after nine run.

Table 3 Reusability of the catalyst in the trimethysilylation of benzyl alcohol with HMDS.

Run	Yield (%)[b]	Sn leached (%)[c]
1	95	0
2	95	0
3	95	0
4	95	0
5	95	0
6	95	0
7	93	0
8	92	0
9	90	0
10	90	0

[a] Reaction conditions: benzyl alcohol (1 mmol), catalyst (10 mg), HMDS (0.6 equiv.), CH_3CN (1 mL), 3 min.; r.t.;[b] Isolated yield.; [c] Determind by ICP.



Scheme 3 Proposed mechanism for the catalytic role of γ-Fe_2O_3@SiO_2-$(CH_2)_3$NH-Sn(n-Bu)$_3$ in trimethylsilylation of alcohols and phenols with HMDS

Experimental

Preparation of silica-coated magnetic nanoparticles (γ-Fe_2O_3@SiO_2):

The maghemite (γ-Fe_2O_3) nanoparticle was synthesized according to a reported procedure.[26] $FeCl_2·4H_2O$ (1.99 g, 10 mmol) and anhydrous $FeCl_3$ (3.25 g, 20 mmol) were dissolved in deionized water (20 mL) separately. Next, mechanically mixing the two iron salt solutions under vigorous stirring at 800 rpm, at room temperature in an argon atmosphere was performed. To maintain the reaction pH balance between 11 and 12, a concentrated solution of NH_4OH (25% w/w, 30 mL) was then added to the stirred solution maintained at room temperature. The resulting black dispersion was continuously stirred for 1 h at room temperature and then heated to reflux for 1 h, after cooling the heated solution to room temperature, 80 mL of ethanol was added, followed by the addition of concentrated ammonia solution 20 mL. The resulting mixture was stirred at 40 °C for 30 min. Subsequently, tetraethyl orthosilicate (TEOS, 20 mL) was charged ino the reaction vessel, and the mixture was continuously stirred at 40 °C for 24 h. The silica-coated magnetic nanoparticles were collected with the aid of a permanent magnet, followed by washing the nanoparticles three times with ethanol (EtOH), water and dried at 100 °C for 12 h. The as-synthesized sample was calcined at 300 °C for 3h.

Synthesis of 3-aminopropyl covalently attached onto the surface of silica-encapsulated magnetic nanoparticles (γ-Fe_2O_3@SiO_2-$(CH_2)_3$-NH_2):[27]

A sample of silica-coated magnetic nanoparticles γ-Fe_2O_3@SiO_2 (500 mg) suspended in a mixture of 150 mL dry toluene containing a stoichiometric amount of 3-aminopropyltrimethoxysilane (92 mg, 0.5 mmol). The mixture was refluxed under argon atmosphere at 100 °C for 48 h. The product was separated with the aid of an external magnet, washed with ethanol, and dried for 5 h at 110 °C.

Synthesis of tributyltin bonded to aminopropyl-functionalized silica-coated magnetic nanoparticles (γ-Fe_2O_3@SiO_2-$(CH_2)_3$NH-Sn(n-Bu)$_3$):

To 1 g γ-Fe_2O_3@SiO_2-$(CH_2)_3NH_2$, in 30 mL deionized water, tributyltin chloride (0.325 g, 1 mmol) in acetone (15 mL) was added dropwise at room temperature over 15 min. The mixture was mechanically stirred for 24 h at room temperature. Subsequently the resulting magnetic nanoparticles were separated with the use of an external magnet next, washed with ethanol then dried at 100 °C for 12 h.

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DOI: 10.1039/C4RA04911J

General procedure for trimethylsilylation of, alcohols and phenols with HMDS in the presence of γ-Fe_2O_3@SiO_2-$(CH_2)_3$NH-Sn(*n*-Bu)$_3$:

To the stirred mixture of alcohol or phenol (1 mmol) and catalyst (10 mg) in acetonitrile (1 mL), HMDS (97 mg, 0.6 mmol), were added. The reaction was then magnetically stirred at room temperature. The progress of the reaction was monitored by Thin Layer Chromatography (*TLC*). Upon completion of the reaction, the catalyst was separated from the reaction mixture using an external magnet, washed with acetonitrile three times to remove all residual products then, dried for reuse in a subsequent run. Distilled water (1 mL) was added to the filtrate and the product was extracted with dichloromethane (2×2 mL). The organic layer was dried over anhydrous sodium sulfate (Na_2SO_4) and filtered to remove any remaining residue. After the evaporation process of the solvent, the products were purified using a short column of silica gel eluted with ethyl acetate/ *n*-hexane (1:4).

Conclusions

In this study the prepared tributyltin catalyst was heterogenized on magnetic nanoparticles and used as a stable and reusable catalyst for mild and efficient trimethylsilylation of hydroxyl groups. Primary, secondary, and tertiary alcohols and phenols were efficiently converted to trimethysilyl ethers with excellent yields and short reaction times. The advantages of this catalyst is the ease of separation from the reaction mixture using a permanent magnet and, its'repeated recyclability.

Acknowledgement

We are thankful to the Tarbiat Modares University for financial support of this work.

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DOI: 10.1039/C4RA04911J

Tributyltin Grafted onto the Surface of 3-Aminopropyl Functionalized γ- Fe_2O_3 Nanoparticles: A Magnetically-recoverable Catalyst for Trimethylsilylation of Alcohols and Phenols

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Heterogenization of tributyltin catalyst on the surface of functionalized magnetic nanoparticles provides a magnetically-recyclable catalyst for trimethylsilylation of alcohols.