Molecular Catalysis 474 (2019) 110357

Contents lists available at ScienceDirect

Molecular Catalysis

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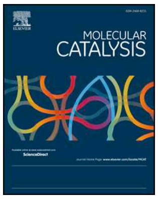

A simple and efficient room temperature silylation of diverse functional groups with hexamethyldisilazane using CeO_2 nanoparticles as solid catalysts

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ARTICLE INFO

Keywords:
Cerium oxide
Hexamethyldisilazane
Nanoparticles
Protection
Silylation

ABSTRACT

In this study, a mild and efficient method is developed for the silylation of diverse functional groups using CeO_2 nanoparticles (n-CeO_2) as solid catalysts with hexamethyldisilazane (HMDS) as silylating agent at room temperature. Alcohols, phenols and acids are silylated to their respective silyl derivatives with faster reaction rate while amines and thiols required relatively longer reaction time. Moreover, the solid catalyst is easily be separated from the reaction mixture and recycled more than five times without any obvious decay in its activity. Powder X-ray diffraction (XRD), transmission electron microscope (TEM), UV–vis diffuse reflectance spectra (UV-DRS) and Raman analyses revealed identical structural integrity, particle size, absorption edge and valence state for the reused solid compared to the fresh solid catalyst.

1. Introduction

Metal oxide nanomaterials have received more attentions in recent years due to their appreciable chemical, physical and electronic properties compared to their bulk analogues [1,2]. These fascinating properties of metal oxide nanomaterials found applications in many fields like environmental remediation, [3,4] energy conversion [5–7], water treatment [8–10], sensor [11–13] and catalysis [14–17]. Ceria (CeO_2) is an important class of family of transition metal based metal oxide which has shown their great potential in many organic transformations such as dehydration of alcohols, [18–20] alkylation of aromatic compounds [21,22], hydration of nitriles [23], synthesis of *N*-alkylamides [24], alcoholysis of amides [25], aerobic oxidations [26,27] and acetylene semihydrogenation [28]. Typically, protection of functional group is a useful strategy in multistep target organic synthesis [29,30]. Conventionally, functional group protection has been performed by different protecting probes. Among them, silylating probes like chlorotrimethylsilane [31], allylsilane [32] and alkylsilane [33] (all of them introduce trimethylsilyl group for protection) gained little attention compared to others. However, aforementioned silylation reagents gave only interim solution but not final due to their toxicity and low yield of product. Markedly, HMDS has emerged as an alternative source and provides some solutions to the above mentioned problems and also produce ammonia as the only by product. Eventhough, HMDS is stable, commercially available and convenient for handling, the poor silylating power is the main drawback for its applicability, since, it requires high temperature and longer reaction time. For these reasons, wide range of catalysts have been employed for activation of HMDS including $(CH_3)_3SiCl$, [34] K-10 montmorilonite [35], $H_3PW_{12}O_{40}$ [36], $Bi(OTf)_3$ [37], $Fe(F_3CCO_2)_3$ [38], I_2 [39], trichloroisocyanuric acid [40], $Zr(OTf)_2$ [41], $LiClO_4$ [42], H-β zeolite [43], *N*-chlorosaccharin [44], nanocrystalline TiO_2-HClO_4 [45] and CMK-5-SO_3H [46]. However, most of the previously reported catalysts were explored in the protection of alcohols and phenols, but acids, amines and thiols were seem to be rarely explored. Therefore, the present work reports the silylation of diverse range of functional groups including alcohols, phenols, acids, amines and thiols with HMDS as silylating agent using n-CeO_2 as solid heterogeneous catalyst at room temperature in short reaction time. This process is viable for broad range of substrates with more functional groups tolerance.

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https://doi.org/10.1016/j.mcat.2019.03.015
Received 6 February 2019; Received in revised form 11 March 2019; Accepted 11 March 2019

2. Experimental section

2.1. Materials and methods

Alcohols, amines, acids, phenols, thiols, HMDS and cerium(IV) oxide nanoparticles (Product Ref. No. 544841) were purchased from commercial suppliers of Sigma Aldrich, Alfa Aesar and Merck and used as received. Bulk cerium(IV) oxide was purchased from Sisco Research Laboratory limited (Product Code 23505), but however, the average particle size was not supplied. Dichloromethane and other solvents were also received from Sigma Aldrich and Merck and used as received without any further purification.

2.2. Reaction procedure

2.2.1. General procedure for silylation of alcohols and phenols with HMDS

In a typical silylation reaction, the reaction flask was charged with 12 mol% of n-CeO_2 (20 mg), 1 mmol of substrate (alcohol or phenol or thiol), 2 mL of solvent and 1 mmol of HMDS. This heterogeneous mixture was stirred for the required time mentioned in Tables 1 and 2 at room temperature. The progress of the reaction was monitored by Agilent 7820 A gas chromatography by sampling aliquots at different time intervals. After completion of the reaction, the mixture was diluted with dichloromethane and filtered. Then, the crude mixture was evaporated to afford the pure product. Later, the product was analyzed by gas chromatography for its purity and selectivity. The as-synthesized products were characterized by Agilent 7820 A gas chromatography coupled with 5977B mass detector to confirm the silylated product. The above described procedure was followed for the silylation of acids and amines according to the conditions shown in the foot notes of the respective Tables. Further, reusability experiments were performed as described above except that the recovered catalyst after the reaction was washed with dichloromethane, dried and reused in the next cycle with fresh reactants.

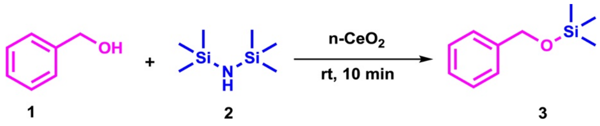
2.2.2. Instrumentation

UV-visible Diffuse Reflectance Spectroscopy (UV-DRS) analyses were carried out by shimadzu UV-2700; ISR-2600 plus instrument in the ranging from 200 to 900 nm. Raman spectra were measured by a InVia, Renishaw, UK with confocal microprobe under ambient conditions with 532 nm as the excitation wavelength. Powder XRD diffraction patterns were measured in the refraction mode in a Philips X'Pert diffractometer using the CuK_α radiation ($\lambda = 1.54178$ Å) as the incident beam, PW3050/60 (2θ) as Goniometer, PW 1774 spinner as sample stage, PW 3011 as detector, incident mask fixed with 10 mm. The size and shape of the n-CeO_2 was confirmed by JEOL JEM 2100 transmission electron microscope (TEM).

3. Results and discussion

In the beginning of our studies, the silylation reaction was optimized by selecting benzyl alcohol (**1**) as a model substrate with HMDS (**2**) as a silylating agent to evaluate the activity of n-CeO_2 as catalyst in the presence of solvent and solvent-free conditions at room temperature. The obtained results are shown in Table 1. Gratifyingly, the silylation of **1** with **2** afforded complete conversion of **1** with complete selectivity of corresponding silyl ether using 12 mol% of n-CeO_2 in dichloromethane as solvent within 10 min (entry 2, Table 1). In contrary, a blank control experiment in the absence of catalyst gave only 11% conversion of **1** under identical conditions (entry 1, Table 1). Further, the activity of n-CeO_2 for silylation of **1** by **2** was studied with various solvents including polar, non-polar as well as under solvent-free conditions. The use of non-polar solvent like toluene resulted in 37% conversion of **1** while with polar solvents such as acetone (74%), ethyl acetate (86%), dioxane (62%), THF (52%) and acetonitrile (92%) provided moderate to quantitative conversion of **1** (entries 3–8, Table 1). These results suggested the involvement of ionic intermediates by the reaction of **1** with HMDS in the presence of n-CeO_2. In addition, conversion of **1** was 97% within 10 min under solvent-free conditions (entry 9, Table 1). Although the conversions of **1** in acetonitrile and under solvent-free conditions were comparable using n-CeO_2 as solid catalyst, dichloromethane was chosen as a solvent since a blank control experiment in dichloromethane exhibited poor conversion of **1**. Further, the effect of n-CeO_2 loading was also investigated in the silylation of **1** and the achieved results are given in Table 1. The observed catalytic data indicated that the conversion of **1** gradually decreased from 100, 93, 79 to 37%, when the catalyst loading reduced from 12, 9, 6 to 3 mol% respectively under similar reaction conditions

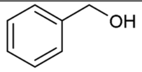
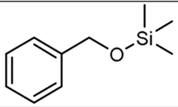
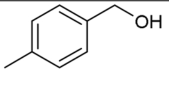
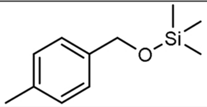
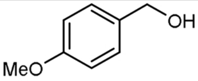
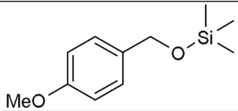
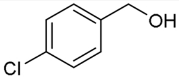
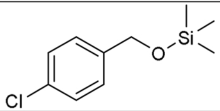
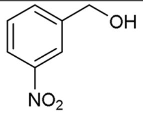
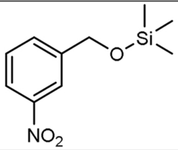
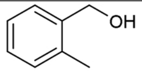
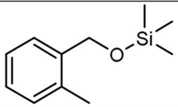
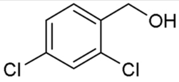
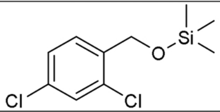
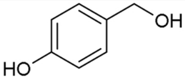
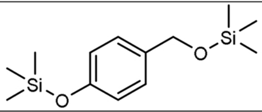
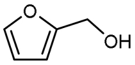
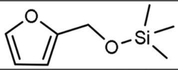
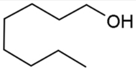
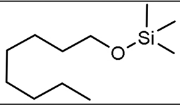
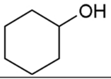
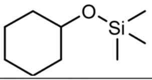
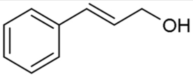
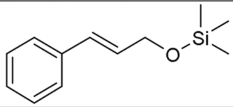
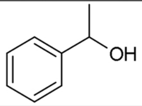
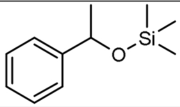
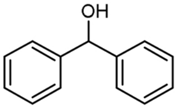
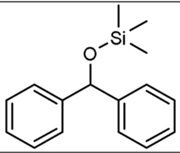
Table 1
Optimization of the reaction conditions for silylation of **1** by **2** using n-CeO_2 as heterogeneous solid catalyst at room temperature.[a]



Entry	Catalyst	Solvent	Conversion[b] (%)
1	–	Dichloromethane	11
2	n-CeO_2	Dichloromethane	100, 93,[c] 79,[d] 37[e]
3	n-CeO_2	Toluene	37
4	n-CeO_2	Acetone	74
5	n-CeO_2	Ethyl acetate	86
6	n-CeO_2	Dioxane	62
7	n-CeO_2	Tetrahydrofuran	52
8	n-CeO_2	Acetonitrile	92
9	n-CeO_2	–	97
10	Bulk-CeO_2	Dichloromethane	17

[a] **Reaction conditions**: **1** (1 mmol), **2** (1 mmol), solvent (2 mL), catalyst (20 mg), 10 min.
[b] Determined by GC using internal standard method.
[c] 9 mol% of n-CeO_2.
[d] 6 mol% of n-CeO_2.
[e] 3 mol% of n-CeO_2.

Table 2
Silylation of diverse functional groups with HMDS in the presence of n-CeO_2 as heterogeneous solid catalyst at room temperature.[a]

Entry	Substrate	Product	Time (min)	Conversion[b] (%)
1			10	100
2			10	100
3			10	100
4			15	100
5			15	100
6			15	100
7			30	100
8			10	100
9			10	100
10			15	100
11			10	100
12			30	99
13			25	>99
14			25	>99

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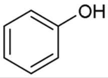
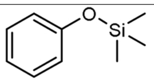
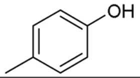
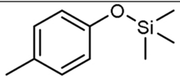
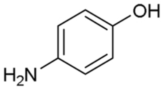
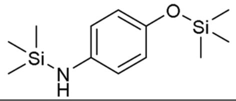
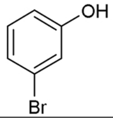
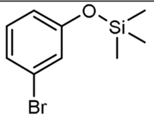
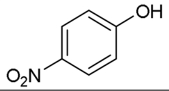
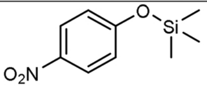
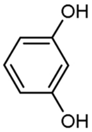
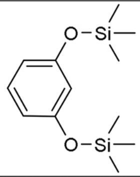
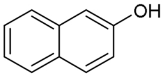
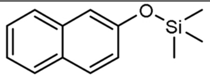
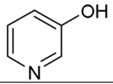
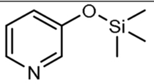
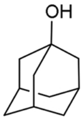
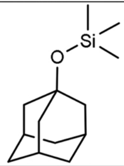
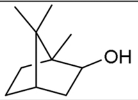
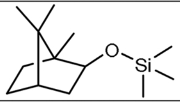
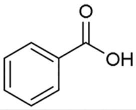
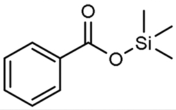
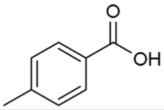
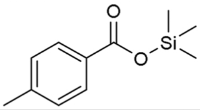
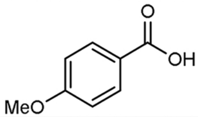
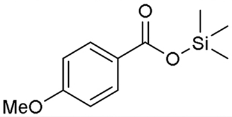
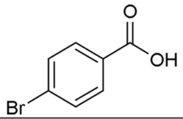
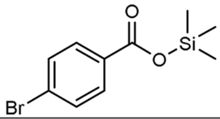
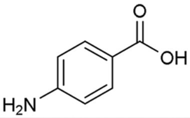
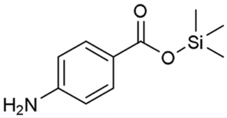
15			10	100
16			10	100
17			10	100
18			20	99
19			20	100
20			10	100
21			10	100
22			10	100
23			60	97
24			40	99
25			15	100
26			15	100
27			15	100
28			15	100
29			15	100

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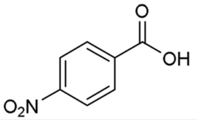
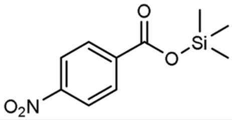
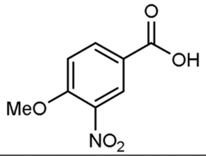
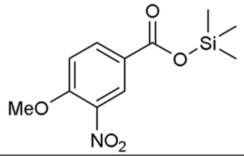
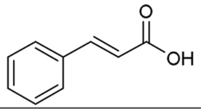
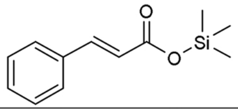
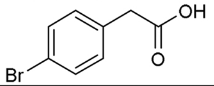
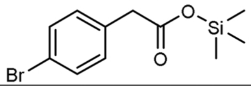
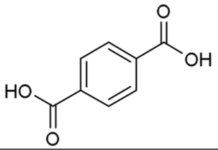
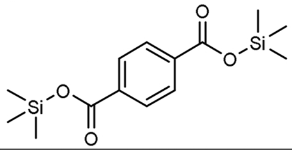
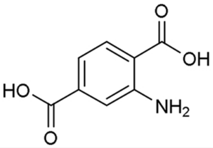
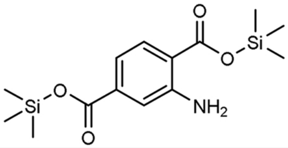
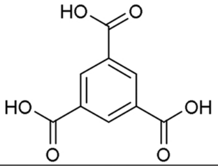
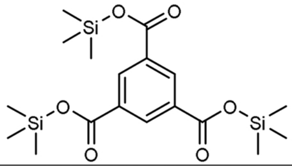
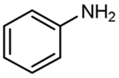
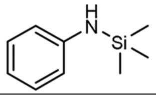
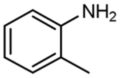
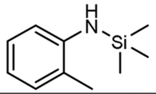
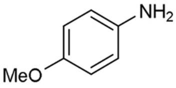
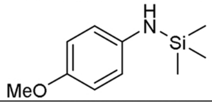
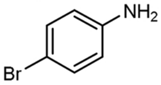
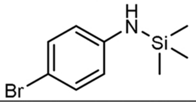
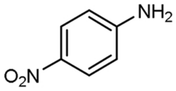
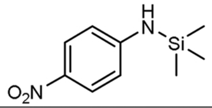
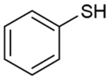
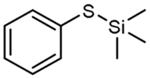
30			20	100
31			25	>99
32			15	100
33			20	>99
34[c]			30	100
35[c]			30	100
36[c]			35	100
37[d]			12[e]	85
38[d]			12[e]	58
39[d]			12[e]	63
40[d]			12[e]	83
41[d]			12[e]	37
42			2[e]	100

[a]**Reaction conditions**: substrate (1 mmol), HMDS (1 mmol), dichloromethane (2 mL), n-CeO_2 (12 mol%); [b]Determined by GC using internal standard method; [c]2 mmol of HMDS was used; [d]**Reaction conditions**: substrate (1 mmol), HMDS (1.3 mmol), dichloromethane (2 mL), n-CeO_2 (15 mol%); [e]Reaction time was in hours.

(entry 2, Table 1). Hence, these catalytic results indicated that 12 mol% of n-CeO_2 is optimum catalyst loading to accomplish complete conversion of **1** within a short reaction time. The activity of n-CeO_2 was compared with its bulk analogue under identical experimental conditions and observing 17% conversion of **1** within 10 min (entry 10, Table 1). These catalytic data suggested that bulk CeO_2 furnished comparatively lower activity and is too far from the conversion achieved with n-CeO_2. These results imply the beneficial advantage of employing n-CeO_2 as solid catalyst for the silylation of **1** with HMDS compared to its bulk form.

These preliminary experiments encouraged us to expand the scope of n-CeO_2 for silylation with other substrates consisting diverse functional groups that include alcohols, phenols, acids, amines and thiols possessing electron withdrawing, donating and sterically crowded substituents. The observed results are shown in Table 2. The silylation of benzyl alcohol and its substituted derivatives furnished complete conversion within 10–15 min of reaction time (entries 1–6, Table 2). Among these substrates, 4-methyl and 4-methoxybenzyl alcohols reacted faster than 4-chloro, 3-nitro and 2-methylbenzyl alcohols. This reactivity difference may be due to the electronic and steric factors of substituents. Moreover, 2,4-dichlorobenzyl alcohol required 30 min to afford complete conversion (entry 7, Table 2) and this behavior may be explained by the steric effect of chloro substituent at C2-position. On other hand, 4-hydroxybenzyl alcohol afforded quantitative conversion within 10 min with the selectivity of 31% alcoholic group silylation and 69% of alcoholic as well as phenolic group silylations (entry 8, Table 2). The silylation reaction of heterocyclic alcohol like furfuryl alcohol, aliphatic alcohol like 1-octanol and alicyclic alcohol like cyclohexanol was efficiently promoted to their respective silyl ethers with complete conversions within 15 min (entries 9–11, Table 2). Further, the silylation of unsaturated alcohol like cinnamyl alcohol to its corresponding silyl ether was achieved in quantitative conversion after 30 min (entry 12, Table 2). In addition, secondary alcohols like 1-phenylethanol and diphenylmethanol required 25 min to afford respective silyl ethers that is slightly slower than primary alcohol (entries 13–14, Table 2).

This protocol was further expanded to the silylation of phenol and its derivatives. The reaction of phenol, *p*-cresol, 4-aminophenol in the presence of n-CeO_2 as solid catalyst with HMDS as silylating reagent afforded respective silyl ethers quantitatively in 10 min (entries 15–17, Table 2). The silylation reaction of 4-aminophenol afforded mixture of silylated products with 30% selectivity to phenolic and 70% selectivity to phenolic as well as amino groups. Similar to the case of silylation of benzyl alcohol, 3-bromo and 4-nitrophenols required slightly longer reaction time than phenol to provide the corresponding silyl ethers (entries 18–19, Table 2). In addition, resorcinol showed quantitative conversion after 10 min under similar conditions with the selectivity of 10 and 90% of mono and disilylated products, respectively (entry 20, Table 2). Also, 2-naphthol and 3-hydroxypyridine were converted into their respective silyl ethers within 10 min (entries 21–22, Table 2). 1-Adamantanol and isoborneol were transformed into their corresponding silyl ethers with 97 and 99% conversions after 60 and 40 min, respectively (entries 23–24, Table 2).

The above wide substrate scope exhibited by n-CeO_2 forced us to expand the catalytic performance of n-CeO_2 in the silylation of carboxylic acids under identical conditions. The obtained results are summarized in Table 2. We were delighted that carboxylic acids bearing electron donating and withdrawing substituents are readily transformed into their corresponding silyl esters in more than 99% conversions within 15–25 min (entries 25–31, Table 2). Remarkably, 4-aminobenzoic acid gave complete conversion with selectivity of 98% silyl ester and only 2% of amine and acid silylated product under optimized conditions. This result indicates chemoselective silylation of one functional group in the presence of other functional groups. 4-Bromophenylacetic acid and cinnamic acid were also reacted facilely with HMDS in the presence of n-CeO_2 to give more than 99% conversions at 20 and 15 min respectively (entries 32-33, Table 2). In contrary, terephthalic acid, 2-aminoterephthalic acid and trimesic acid required slightly excess HMDS (2 mmol) to reach complete conversion under identical catalyst loading (12 mol%) within 30–35 min (entries 34-36, Table 2).

Later, the present method was further tested with amine and its derivatives and the results are given in Table 2. The activity of n-CeO_2 for amine silylation was relatively slower compared to the above tested functional groups. Therefore, the silylation of aniline and its substituted anilines gave low to moderate conversions with complete selectivity of their corresponding silylated products after 12 h (entries 37-41, Table 2). Finally, thiophenol was also successfully silylated under identical reaction conditions and affording complete conversion after 2 h (entry 42, Table 2). The slower reactivity of amines and thiol with HMDS indicated the poor affinity of silicon with these substrates.

Reusability experiments are often considered as a proof of concept to establish the stability of a heterogeneous catalyst. This experiment also provides valuable information about nature of active sites on repeated cycles. In this aspect, n-CeO_2 was easily recovered from the reaction mixture through centrifugation and washed three times with fresh dichloromethane then dried at 70 °C for 30 min. This dried catalyst was used in the subsequent cycles with the fresh reactants by following identical experimental procedure. The observed catalytic results showed that n-CeO_2 is reusable for more than five cycles with no apparent decay in its activity (Fig. 1).

Scheme 1 shows the possible mechanistic pathway for the silylation of diverse functional groups examined in this study. Initially, HMDS was activated by oxygen atoms of n-CeO_2 through coordination with Si atom. Thereafter, nucleophiles attack the activated HMDS with the help of cerium to produce silylated products along with the liberation of ammonia as sole by product which is confirmed by its strong and pungent smell at the end of the reaction from the reaction mixture.

Table 3 provides the comparison of the present catalyst with earlier reported precedents. These results indicate that the present catalyst exhibits some benefits compared to earlier reported methods. Some of the salient features of using n-CeO_2 as a solid catalyst for the silylation of **1** are shot reaction time, readily available commercial catalyst, can be prepared in the laboratory without any tedious procedures and the use of mild reaction conditions. In addition, this work clearly illustrates the wide applicability of this method for wide range of functional groups to facilely covert to their respective silylated compounds.

UV-Visible DRS analyses were performed for the fresh, recovered and six times used n-CeO_2 catalysts and the attained results are

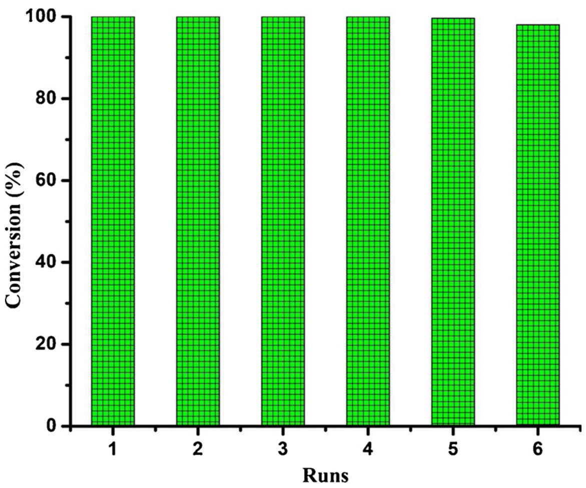
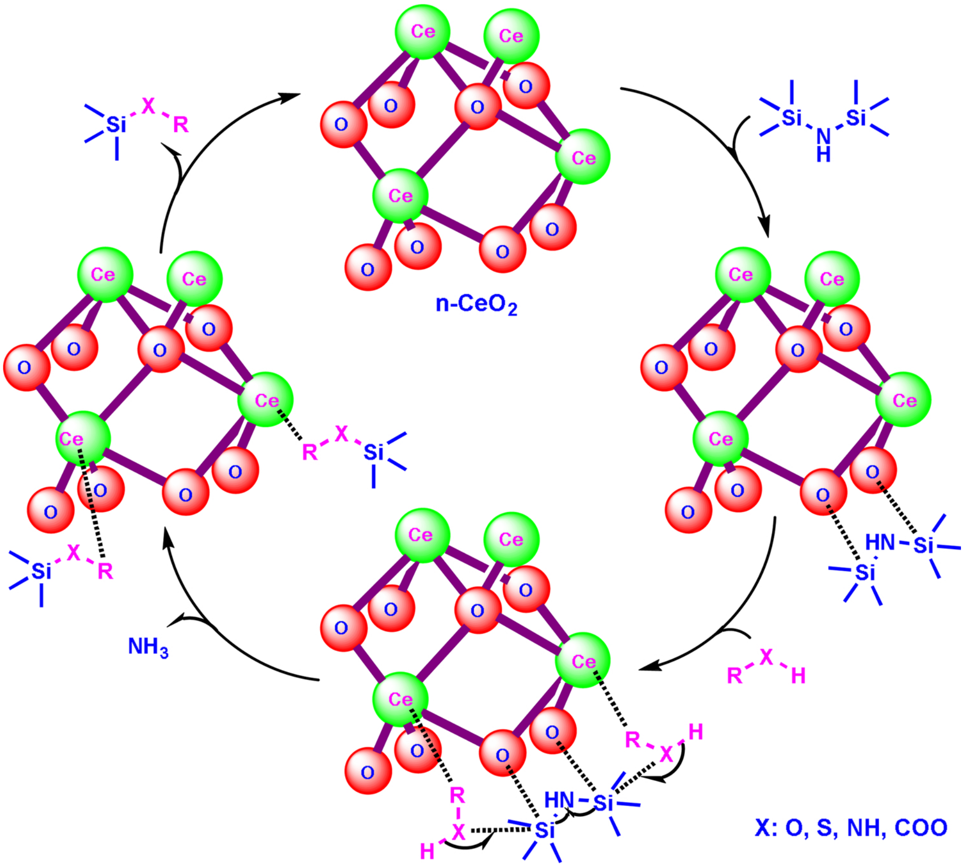


Fig. 1. Recyclability of n-CeO_2 catalyst for the silylation of **1** with HMDS.



Scheme 1. Possible mechanism for n-CeO_2 catalyzed silylation of various functional groups with HMDS.

presented in Fig. 2. These results suggest that the absorption edge for fresh n-CeO_2 exhibits at around 410 nm. In addition, the recovered and six times used n-CeO_2 catalysts showed no significant changes in the absorption edges compared to the fresh n-CeO_2 sample. These results confirm that the n-CeO_2 solid catalyst maintains its structural properties in the silylation of **1** under identical conditions. On other hand, no evidences were found for the reduction of Ce(IV) to Ce(III).

The structural integrity of fresh n-CeO_2 and six times used catalysts was ascertained by powder XRD studies. Fresh n-CeO_2 catalyst shows diffraction peaks at 2θ value around 29, 33 and 49 which can be assigned to (111), (200), (220) reflections (Fig. 3) corresponding to the face-centred cubic phase. Comparison of powder XRD pattern between fresh and the recovered and six times used n-CeO_2 catalysts reveals identical crystalline pattern. However, the intensity of the peaks was reduced slightly in the recovered and six times used catalysts than with fresh sample. This may be due to the adsorption of some products on the surface of six times used n-CeO_2. In any case, the integrity of the catalyst is retained during the silylation reaction. In addition, the cerium content of the fresh and six times used samples were measured by ICP-OES and observing no differences between these two samples.

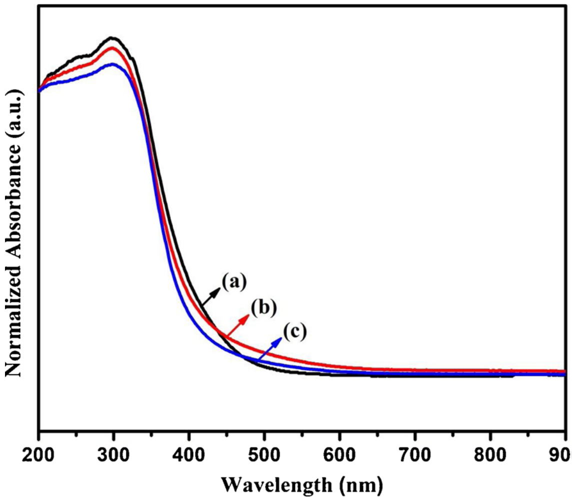


Fig. 2. UV-DRS spectra of (a) fresh, (b) recovered after the reaction and (c) six times used n-CeO_2.

Table 3

Comparison of the activity of n-CeO_2 with previously reported catalysts for the silylation of **1** with HMDS at room temperature.

Entry	Catalyst (mg)	Solvent	Substrate : HMDS	T (°C)	Time (min)	Yield (%)	Reuse	Ref.
1	$Fe(F_3CCO_2)_3$ (10)	–	1:1.5	r.t.	10	95	3	[38]
2	Nafion SAC-13 (50)	–	1:1	r.t.	4	99	4	[47]
3	TiO_2-$HClO_4$ (5)	CH_3CN	1:0.75	r.t.	1	97	5	[45]
4	Fe_3O_4@ZrO_2-Pr-SO_3H (10)	–	1:0.7	r.t.	6	99	9	[48]
5	Al(OH)(BDC) (50)	Toluene	1:1	r.t.	360	99	2	[49]
6	TiO_2 NPs (5)	CH_3CN	1:0.75	r.t.	5	95	3	[50]
7	Fe_3O_4@CeO_2/SO_4^{2-} (7)	–	1:0.7	r.t.	15	93	3	[51]
8	n-CeO_2 (20)	CH_2Cl_2	1:1	r.t.	10	99	5	Present Work

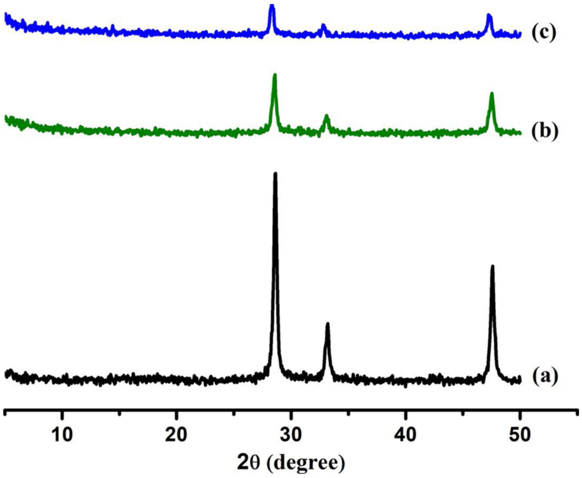


Fig. 3. Powder XRD patterns of (a) fresh, (b) recovered after the reaction and (c) six times used n-CeO_2.

This experiment rules out the possibility of cerium leaching to the solution under the present experimental conditions, thus confirming the stability of catalyst.

Furthermore, the fresh and six cycles used n-CeO_2 solid catalysts were analyzed by TEM analysis and the observed images are given in Fig. 4. TEM measurements indicated that the average particle size of fresh n-CeO_2 sample was in the range of 22–24 nm. In addition, the average particle size of six times used n-CeO_2 samples was not altered during the course of silylation reaction. The analysis of the six times used catalyst by TEM images indicated that the particles are not agglomerated under the present experimental conditions.

Fig. 5 shows the Raman spectra of the fresh and five times used n-CeO_2 solids. The strong signal around 457 cm^{-1} is due to the fluorite type of vibration of Ce(IV) and interestingly no signal is found around 605-610 cm^{-1} concerning to the oxygen vacancies correlated to the existence of Ce^{3+}. These results indicate that the valence state of Ce in n-CeO_2 is in +4 state in the fresh sample. Similarly, the six times used n-CeO_2 show identical signal as that of the fresh solid suggesting the retainment of structural integrity of n-CeO_2 during the silylation reaction.

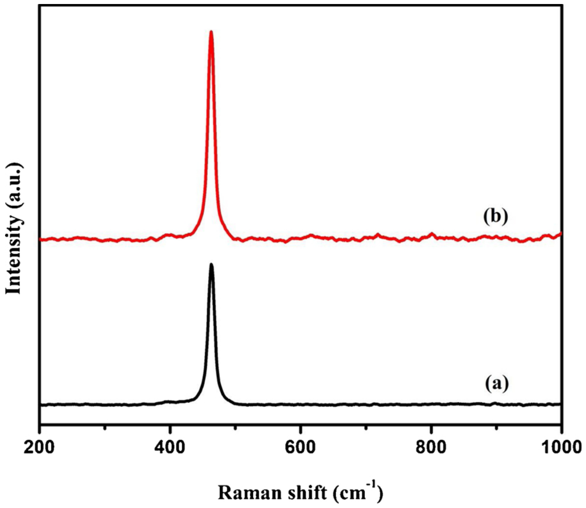


Fig. 5. Raman spectra of (a) fresh and (b) six times used n-CeO_2.

4. Conclusions

In summary, we have shown that n-CeO_2 is an efficient catalyst for the silylation of diverse functional groups with HMDS at room temperature within a short reaction time. Although alcohols, phenols and carboxylic acids exhibited much faster reaction rate while amines and thiol reacted with slower rate. This difference in the activity was due to the poor affinity of silicon with amines and thiol. Moreover, n-CeO_2 exhibited excellent catalytic performance, more functional group tolerance and very broad substrate scope. In addition, n-CeO_2 was easily recovered and reused for six cycles without significant decay in its performance.

Acknowledgements

A.D.M. is grateful to the University Grants Commission, New Delhi, for the award of Assistant Professorship under its Faculty Recharge Program. A.D.M. also acknowledges financial Support from the Science and Engineering Research Board, New Delhi, India through EMR Project (EMR/2016/006500).

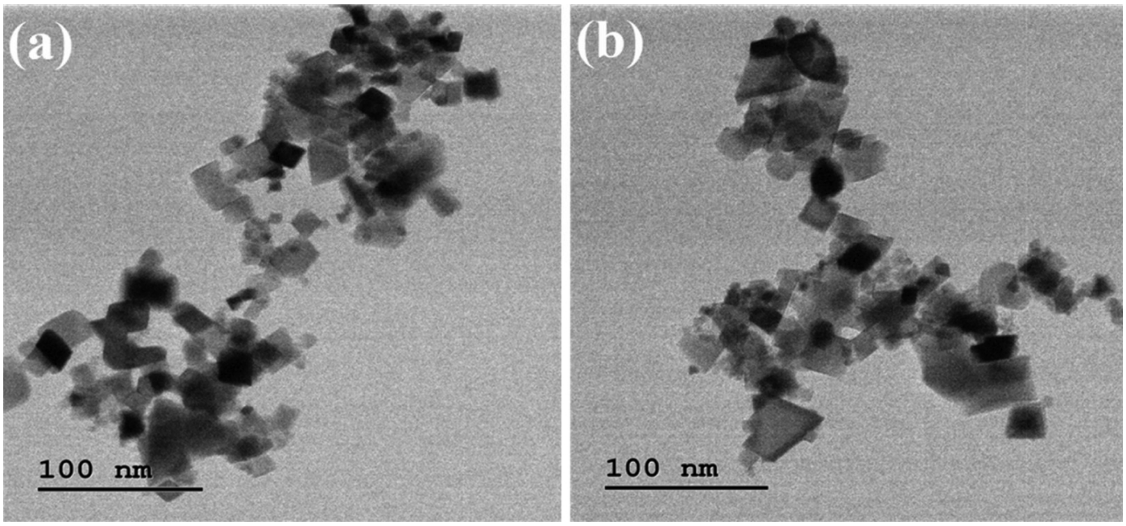


Fig. 4. TEM images of (a) fresh and (b) six times used n-CeO_2.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2019.03.015.

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