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Application of a novel nano-immobilization of ionic liquid on an MCM-41 system for trimethylsilylation of alcohols and phenols with hexamethyldisilazane

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Abstract
3-[(3-(Trisilyloxy)propyl)chloride]-1-methylimidazolium tribromide ionic liquid supported on MCM-41 [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3 as a novel heterogeneous nano-catalyst was easily prepared and characterized using FT-IR spectroscopy, scanning electron microscopy, X-ray diffraction, thermogravimetric analysis, differential thermal analysis, and differential thermogravimetric analysis. This catalyst was successfully applied for selective trimethylsilylation of various alcohols (primary, secondary, and tertiary alcohols) and also various phenols using hexamethyldisilazane in dichloromethane at room temperature to their corresponding trimethylsilyl (TMS) ethers. This method has a lot of advantages such as short reaction time, good to excellent yield of products, and ease of recovering and reusing the catalyst.

Keywords MCM-41 · Phenols · Immobilized ionic liquid · Alcohol · Trimethylsilylation

Introduction

Homogeneous catalysts have higher catalytic activities in proportion to heterogeneous catalyst, because homogeneous catalysts have better solubility in reaction media. On the other hand, one of the biggest disadvantage of such catalysts is the recycling is often time-consuming and tedious [1]. Also, when these catalysts are

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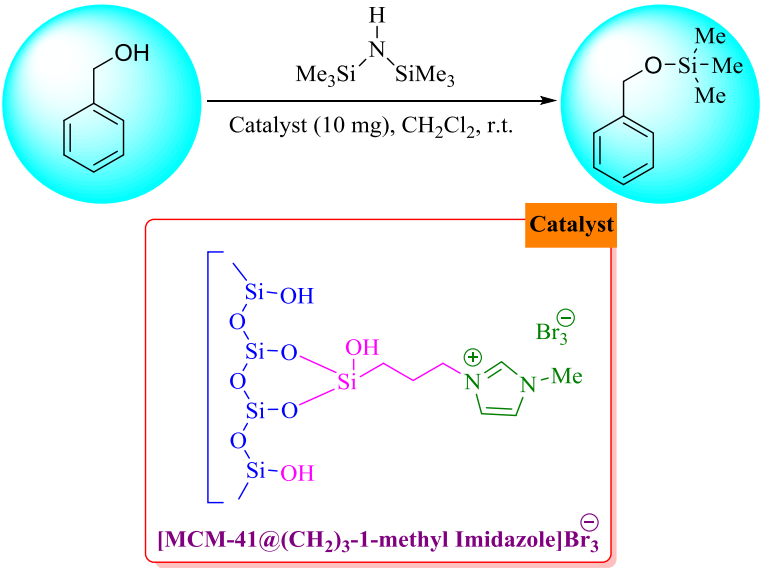
used, the product pollution is observed. Hence, heterogeneous catalysis is favored due to ease of handling and simple and convenient separation [2–6]. Nanoparticles are reusable, readily available, efficient, and have high surface area resulting in high catalyst loading capacity [7]. One of the best advantages of nanoparticles in proportion to other heterogeneous catalysis is that nanoparticles and magnetic nanoparticles can be separated from the reaction medium.

The selective protection of the hydroxyl groups (–OH) by the formation of silyl ethers during a multi-step synthetic process is an extremely important step in modern organic reactions and natural products. Various procedures have been reported for protection of hydroxyl groups such as tetrahydropyranylation, trimethylsilylation, acetylation, and methoxymethylation [8, 9]. Among of the various procedure available for the protection of this hydroxy groups, trimethylsilylation with hexamethyldisilazane (HMDS) is one of the important options; this is because the procedure has several advantages such as easy installation, low cost, remarkable stability, and compatibility under various reaction conditions and reagents. One of the problems of using HMDS in protection groups is its low silylating power in the absence of a suitable catalyst. Hence, several catalysts have been reported for increasing the silylating power of HMDS such as $LiClO_4$ [10], $InBr_3$ [11], $CuSO_4.5H_2O$ [12], iodine [13], $ZrCl_4$ [14], $Fe(TFA)_3$ [15], poly(*N*-bromobenzene-1,3-disulfonamide) and *N,N,N,N*-tetrabromobenzene-1,3-disulfonamide [16], (*n*-Bu_4N)Br [17], sulfonic acid-functionalized nanoporous silica [18], zirconium sulfophenyl phosphonate [19], Pd [20], Fe_3O_4 [21], $HClO_4$–SiO_2 [22], $ZrO(OTf)_2$ [23], $PhMe_3N^+Br^-$ [24], $LaCl_3$ [25], K-10 montmorillonite [26], $(CH_3)_3SiCl$ [27], trichloroisocyanuric acid (TCCA) [28], $LiClO_4$–SiO_2 [29], sulfamic acid [30], poly(4-vinylpyridinium tribromide) [31], H_5IO_6/KI [32], 1,3-dichloro-5,5-dimethylhydantoin (DCH) and/or trichloromelamine (TCM) [33], and $MgBr_2.OEt_2$ [34]. Although various procedures and catalysts for the trimethylsilylation of various alcohols are known, most of the reported procedures have one or more of the following drawbacks: some of the reagents are expensive and toxic, long reaction times, low selectivity, low yields, the use of large amount of catalyst, performances under certain special conditions, drastic reaction conditions, or tedious work up. Hence, the introduction of new procedures to circumvent these problems is still in demand.

Mesoporous materials such as MCM-41 and MCM-48 were discovered by Mobil Oil Company researchers in 1992. MCM-41 plays an important role in chemistry because of its big pore volume, large and uniform pore sizes, ultrahigh surface areas, and rich silanol groups in the inner walls. The structure of MCM-41 is in the form of a hexagonal arrangement of the mesopores and has space group *p* 6 mm [35, 36].

In continuation of our studies toward development of new and cleaner methods for organic transformations [37–41], in this research, we describe the preparation, physicochemical characterization and application of 3-[(3-(trisilyloxy)propyl)chloride]-1-methylimidazolium tribromide ionic liquid supported on MCM-41 [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3 as a highly efficient and novel heterogeneous nanocatalyst for the selective trimethylsilylation of various alcohols and phenols using HMDS at room temperature (Scheme 1).



Scheme 1 Trimethylsilylation of alcohols and phenols with HMDS-catalyzed [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3

Experimental

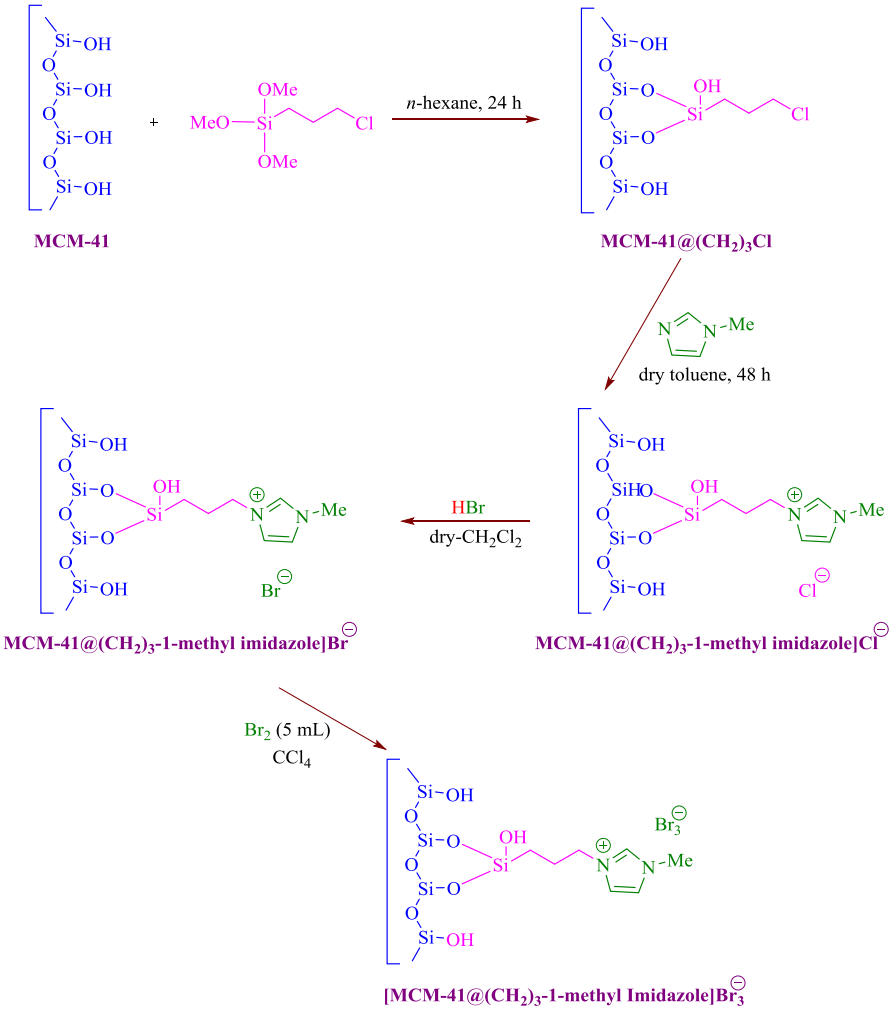
Materials

All chemicals were purchased from Merck or Fluka chemical companies. Thin-layer chromatography (TLC) was performed on pre-coated aluminium plates (silica gel 60 F254, Merck). Infrared (IR) spectra of the compounds were obtained on a Perkin Elmer spectrometer version 10.03.06 using a KBr disk. The phases present in the magnetic materials were analyzed using a powder X-ray diffraction (XRD) system (Philips, Holland, model X0 Pert) with X' Pert and CuKα1 radiation (λ = 1.5401 Å), and the X-ray generator was operated at 40 kV and 30 mA. Diffraction patterns were collected from 2 h = 20–80°. Transmission electron micrographs of the magnetic nanoparticles were taken on a Philips CM 120 transmission electron microscopy (TEM) instrument.

General procedure for the preparation of [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3 as a novel heterogeneous nanocatalyst

At first, nano-MCM-41@$(CH_2)_3$Cl was produced by adding 3-chloropropyl(trimethoxy)silane (10 mmol, 1.98 g) in *n*-hexane (25 mL) to MCM-41 (2.0 g) with stirring under reflux conditions for 24 h at 40 °C. Then, nano-MCM-41@$(CH_2)_3$Cl was filtered, washed with ethyl acetate, and dried under vacuum at 50 °C [35]. In the next step, 1-methylimidazole (0.340 g, 5 mmol) in 50 mL of dry toluene was added to the 1 g of the nano-MCM-41@$(CH_2)_3$Cl and the mixture was

refluxed for 48 h at 90 °C. After the reaction was completed, the resulting solid was filtered, washed with ethanol, and dried to create the [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Cl [35]. A solution of hydrobromic acid (5 mmol) in dry dichloromethane (10 mL) was added drop-wise to 1 g of the [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Cl and the reaction mixture was stirred for 1 h. After the reaction, the solvent was removed under vacuum to give [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br. Then, a solution of dibromine (5 mL) was added drop-wise to the [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br (1 g) in CCl_4 (50 mL) and the reaction mixture was stirred for 24 h. Finally, the solvent was removed under vacuum and [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3 as a



Scheme 2 The synthesis of 3-[(3-(trisilyloxy)propyl)chloride]-1-methylimidazolium tribromide ionic liquid supported on MCM-41 [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3

pale orange was obtained after filtering, washing with CCl_4 (3 × 10 mL) and drying (Scheme 2).

General procedure for trimethylsilylation with HMDS catalyzed by [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3

To a mixture of alcohol or phenol (1 mmol) and HMDS (2 mmol) in CH_2Cl_2 (5 ml) was added 10 mmol of [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3 with stirring at room temperature for the appropriate time (Table 3). The progress of the reaction was monitored by TLC. At the end of the reaction, the solvent was evaporated, Et_2O (10 mL) was added, and the catalyst was filtered. The filtrates were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to afford the crude product.

Results and discussion

Characterization of [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3 as a novel heterogeneous nanocatalyst

Recently, Hajian and coworkers reported an excellent range of imidazole-based ionic liquid stabilized on MCM-41 as an efficient heterogeneous catalysts for the synthesis of epoxidation of various olefins in the presence of *tert*-BuOOH in 1,2-dichloroethane under reflux [42]. Hence, our team has reported for the first time the synthesis of 3-[(3-(trisilyloxy)propyl)chloride]-1-methylimidazolium tribromide ionic liquid supported on MCM-41 [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3 as a novel heterogeneous nanocatalyst for selective trimethylsilylation of various alcohols and phenols using HMDS in CH_2Cl_2 at room temperature. The structure of 3-[(3-(trisilyloxy)propyl)chloride]-1-methylimidazolium tribromide ionic liquid supported on MCM-41 [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3 as a novel heterogeneous nanocatalyst was studied and characterized by FT-IR, scanning electron microscopy (SEM), XRD, thermogravimetric analysis (TGA), differential thermal analysis (DTA), and differential thermogravimetric (DTG) analysis.

The IR spectrum of [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3 (Fig. 1) shows characteristic bands at 1460 and 1632 cm^{-1} assigned to C=C and C=N bonds (imidazole ring), respectively. The strong absorption at 1089 cm^{-1} is due to the Si–O stretching in the Si–O–Si structure. Individually, the absorption peak at 2926 cm^{-1} is assigned to the stretching vibration of C–H groups. Additionally, the absorption band at 3421 cm^{-1} is assigned to O–H stretching of the surface silanols of the MCM-41. Also, the strong absorption at 807 cm^{-1} is related to the Br group.

The nanostructure of [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3 is confirmed by SEM (Fig. 2). The SEM micrograph clearly proved that the particles were nano-sized. As shown in Fig. 2, [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3 consist of relatively small, nearly spherical particles, with an average size of 40 nm.

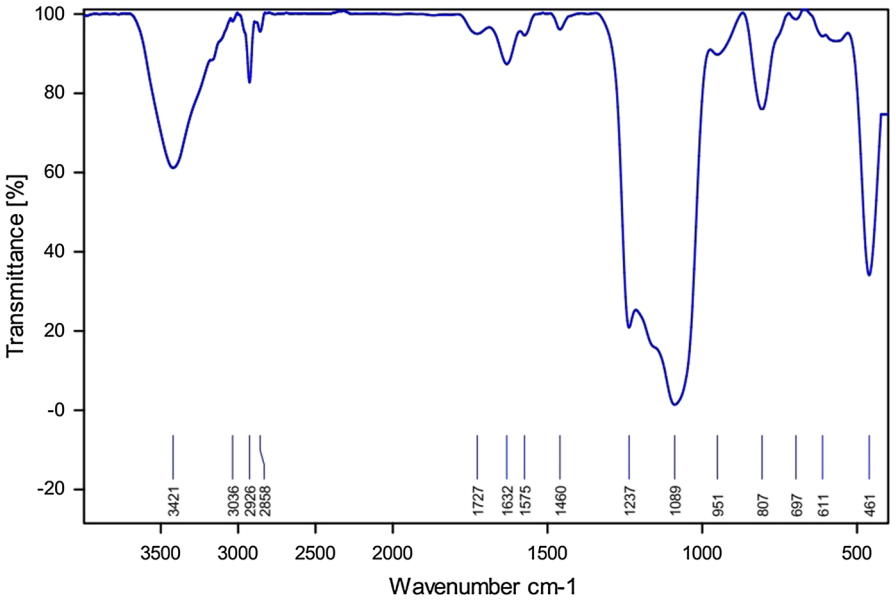


Fig. 1 IR spectrum of [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3

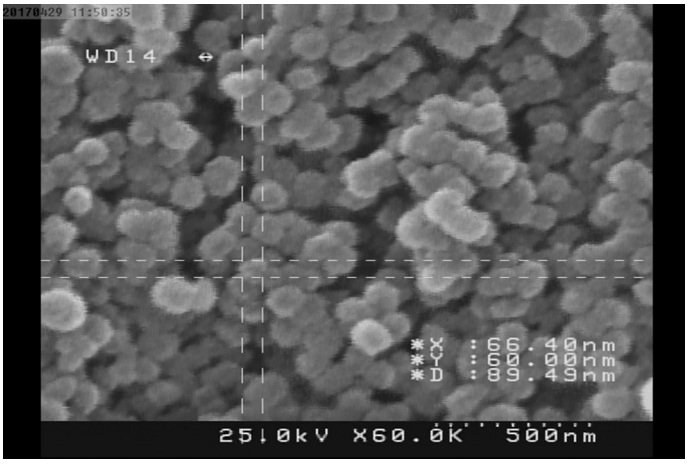


Fig. 2 The SEM micrographs of [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3

TGA, DTA), and DTG of [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3 as a heterogeneous nanocatalyst show the mass loss of organic material as it decomposes upon heating (Fig. 3).

The major weight loss from the [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3 at 100 °C is due to the removal of physically adsorbed organic solvents, which were applied during synthesis of the catalyst. The weight loss of about 13% at 200 °C is due mainly to the thermal decomposition of imidazole. Also, the weight loss of

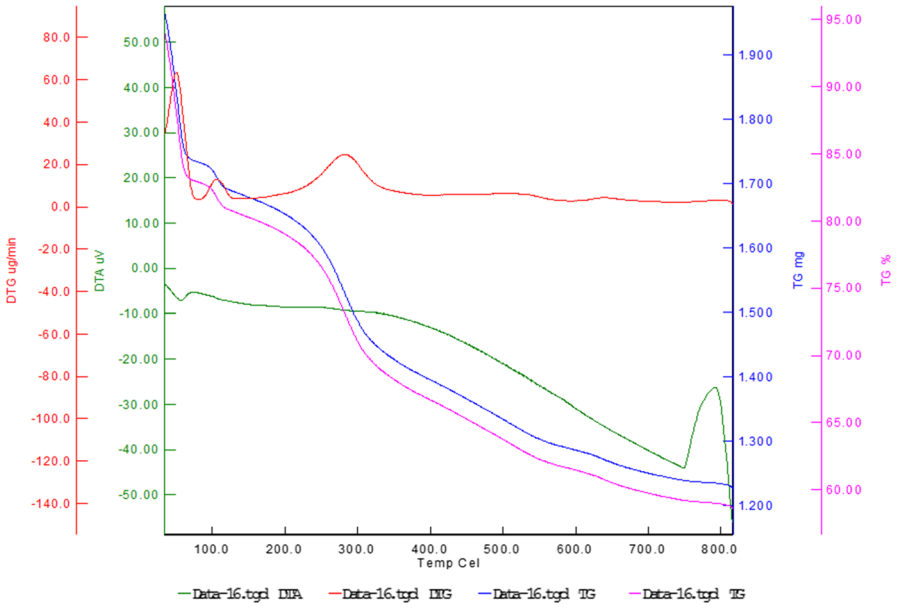


Fig. 3 TGA, DTA, and DTG of [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3

about 23% at 300 °C is attributed to the thermal decomposition of the catalyst. As a consequence, the three-step weight loss of the catalyst is visible and the catalyst decomposes after 300 °C.

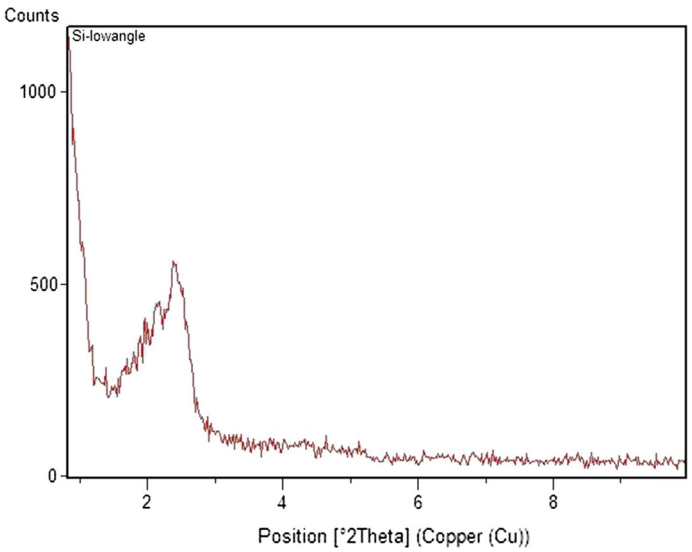


Fig. 4 XRD patterns of [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3

The structural properties of synthesized [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3 were analyzed by XRD (Fig. 4). The XRD pattern of the [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3 was considered in a range of 0°–10°. As can be seen in Fig. 4, the XRD pattern displays diffraction lines of high crystalline nature. The crystalline size of the catalyst is 38 nm, as calculated using the Scherrer equation ($D = K\lambda/\beta \cos \theta$). D is the crystalline size, K is the shape factor, corresponding to 0.9, β is the broadening of the diffraction line measured at half of its maximum intensity in radians, λ is the wavelength of the X rays, and q is the Bragg diffraction angle.

Application of [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3 as a novel heterogeneous nanocatalyst for selective trimethylsilylation of various alcohols

The synthesis route for the [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3 nanocatalyst is shown in Scheme 2. The catalytic activity of [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3 was investigated in the trimethylsilylation of alcohols and phenols with HMDS. For this purpose, to optimize the reaction conditions, the condensation reaction between 4-methoxy phenol (1 mmol) with HMDS (2 mmol) was chosen as a typical condition, and different amounts of [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3 as a nanocatalyst in various solvent at room temperature were studied (Table 1). As can be seen in Table 1, the best result was obtained when the reaction was carried out in the presence of 10 mg of [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3 as nanocatalyst at room temperature in CH_2Cl_2 (Table 1, entry 4). When the reaction was carried out by increasing the amount of the nanocatalyst, no improvement in the yield was observed (Table 1,

Table 1 Result based on the amount of the catalyst and various solvents for the trimethylsilylation of 4-methoxy phenol with HMDS

Entry	Catalyst loading (mg)	Solvent (5 mL)	Reaction time (min)	Yield (%)[a]
1	Catalyst-free	Solvent-free	120	Trace
2	5	CH_2Cl_2	75	32
3	7	CH_2Cl_2	50	45
4	10	CH_2Cl_2	40	93
5	15	CH_2Cl_2	40	90
6	10	Solvent-free	75	90
7	10	CH_3CO_2Et	75	15
8	10	CH_3CN	75	25
9	10	*n*-Hexane	75	30
10	10	Tetrahydrofuran	60	40
11	10	Diethyl ether	100	50

Reaction conditions: 4-methoxy phenol (1 mmol), HMDS (2 mmol)

[a]Isolated yield

entry 5). When the reaction was carried out with 10 mg of catalyst among various solvents such as CH_2Cl_2, CH_3CO_2Et, CH_3CN, *n*-Hexane, THF, and diethyl ether, the highest yield and shortest reaction time were observed in CH_2Cl_2 (Table 1, entries 7–11).

In the next study, we examined the trimethylsilylation of the 4-methoxy phenol (1 mmol) with different amounts of the HMDS in the presence 10 mg of [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3 in CH_2Cl_2 at room temperature (Table 2). As can be seen in Table 2, the reaction was carried out with different amounts of the HMDS such as 2, 2.5, and 3 mmol. The best result was obtained when the reaction was carried out with 2 mmol of HMDS.

After optimization of the reaction conditions, the investigation was followed by performing the reaction with various hydroxyl groups including aliphatic and aromatic alcohols and various phenols with HMDS in CH_2Cl_2 at room temperature. The trimethylsilylation of various alcohols and phenols was obtained in short reaction times with high yields. As shown in Table 3, a variety of alcohols (primary, secondary, and tertiary alcohols) and as well as phenols were successfully employed to prepare the corresponding silyl ether in high yields and short reaction time. Therefore, the results revealed that this methodology is efficient and for a wide range of hydroxyl groups of alcohols and phenols.

A probable mechanism has been shown for trimethylsilylation alcohols with [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3 in Scheme 3. As can be seen in Scheme 3, initially, [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3 led to release of Br^+, which can act as an electrophilic species, and react with HMDS to give intermediate **A**. Similarly, intermediate **A** reacts with one mole of alcohol to afford their corresponding trimethylsilyl (TMS) ethers. Then, another silyl portion of the HMDS again forms an intermediate **B** with the [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3. Again, intermediate **B** reacts with one mole of alcohol to afford their corresponding TMS ethers, and another silyl portion of the HMDS again forms an intermediate **C** with the [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3. Finally, intermediate **C** gives gaseous NH_3 and the recycling of [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3 (Scheme 3).

To compare the efficacy of our presented method with some reported methods for the silylation reactions, we have presented the results of our catalyst to attain the

Table 2 Result based on the amount of HMDS used for the trimethylsilylation of 4-methoxy phenol in CH_2Cl_2 at room temperature

Entry	HMDS (mmol)	Solvent (5 mL)	Reaction time (min)	Yield (%)[a]
1	2	CH_2Cl_2	40	93
2	2.5	CH_2Cl_2	45	90
3	3	CH_2Cl_2	45	90

Reaction conditions: 4-methoxy phenol (1 mmol), HMDS (2, 2.5, and 3 mmol) in CH_2Cl_2 at room temperature

[a]Isolated yield

Table 3 Trimethylsilylation of alcohols and phenols using HMDS under the influence of [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3

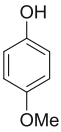
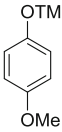
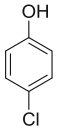
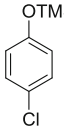
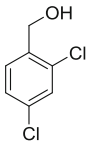
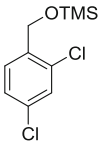
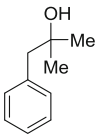
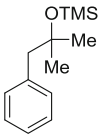
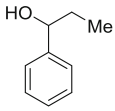
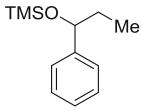
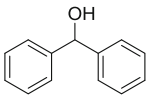
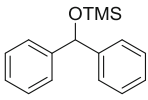
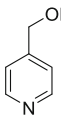
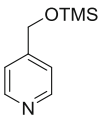
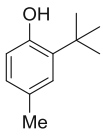
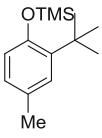
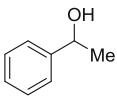
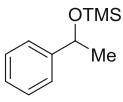
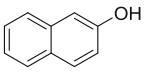
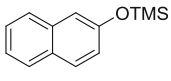
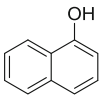
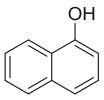
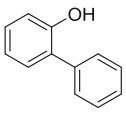
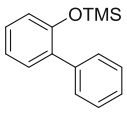
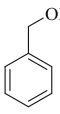
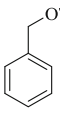
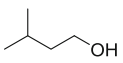
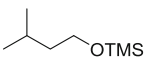
Entry	Substrate	Product	Reaction time (min)	Yield (%)[a]
1			40	93
2			35	96
3			30	95
4			30	93
5			30	93
6			50	90
7			50	88
8			70	93
9			45	90
10			30	91

Table 3 continued

Entry	Substrate	Product	Reaction time (min)	Yield (%)[a]
11			35	89
12			30	93
13			40	94
14			35	94
15			25	92
16			25	90

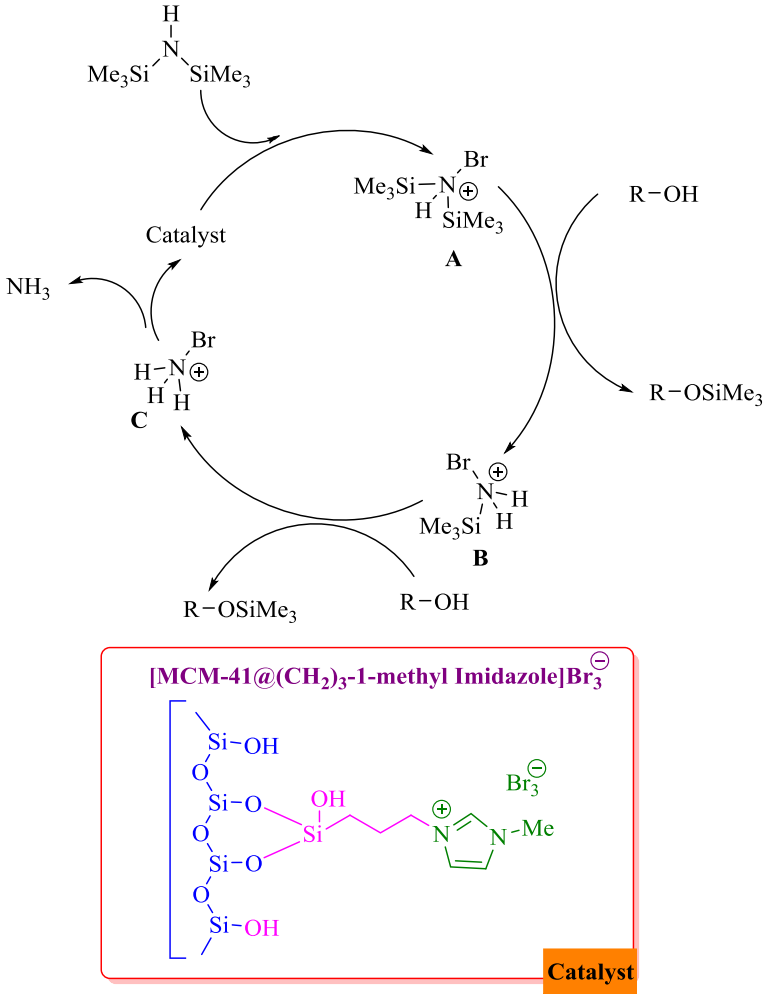
[a] Isolated yield

condensation of trimethylsilylation of benzyl alcohol with HMDS with some of those reported in the literature. As can be seen in Table 4, the [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3 nanocatalyst improves synthesis of the product.

One of the best advantages of heterogeneous catalysis is that it can be separated from the reaction medium. Hence, the reusability of the [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3 was checked by the condensation of benzyl alcohol with HMDS under the same reaction conditions (Fig. 5). As can be seen in Fig. 5, the catalyst can be reused and recycled for seven runs without any significant loss of its initial catalytic activity.

Conclusion

The 3-[(3-(trisilyloxy)propyl)chloride]-1-methylimidazolium tribromide ionic liquid supported on MCM-41 [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3 as a novel heterogeneous nanocatalyst was prepared and characterized by FT-IR, SEM, XRD, TGA, DTA, and DTG analysis. Catalytic applications of the described



Scheme 3 The probable mechanism for the synthesis of TMS ethers using [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3

catalyst were investigated for selective silylation of various alcohols and phenols using HMDS to prepare the corresponding silyl ether in dichloromethane at room temperature. Using this procedure, primary, secondary, and tertiary alcohols and also phenols were protected in good to excellent yields with short reaction times. The salient features of this methodology are cheap processing, easy synthesis of the heterogeneous nanocatalyst, easy work-up procedure, and ease of recovery from the reaction mixture.

Table 4 Comparison of the results obtained for the trimethylsilylation of benzyl alcohol catalyzed by [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3 with those obtained by recently reported catalysts

Entry	Catalyst	Conditions	Time (min)	Yield (%)	References
1	PBBS[a]	r.t., CH_2Cl_2	90	90	[16]
2	TBBDA[b]	r.t., CH_2Cl_2	30	30	[16]
3	Sulfonic acid@nanoporous silica	r.t., CH_2Cl_2	80	100	[18]
4	$HClO_4$–SiO_2	r.t., CH_3CN	2	98	[22]
5	$ZrO(OTf)_2$	r.t., CH_3CN	1	92	[23]
6	$LaCl_3$	r.t., CH_2Cl_2	3 h	91	[25]
7	TCCA[c]	r.t., CH_2Cl_2	4 h	90	[28]
8	$MgBr_2OEt_2$	r.t., solvent-free	5	98	[34]
9	$H_3PW_{12}O_{40}$	55–60 °C, neat	23	90	[43]
10	[Nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3	r.t., CH_2Cl_2	25	95	–

[a]Poly(*N*-bromobenzene-1,3-disulfonamide)

[b]*N*,*N*,*N*-tetrabromobenzene-1,3-disulfonamide

[c]Trichloroisocyanuric acid

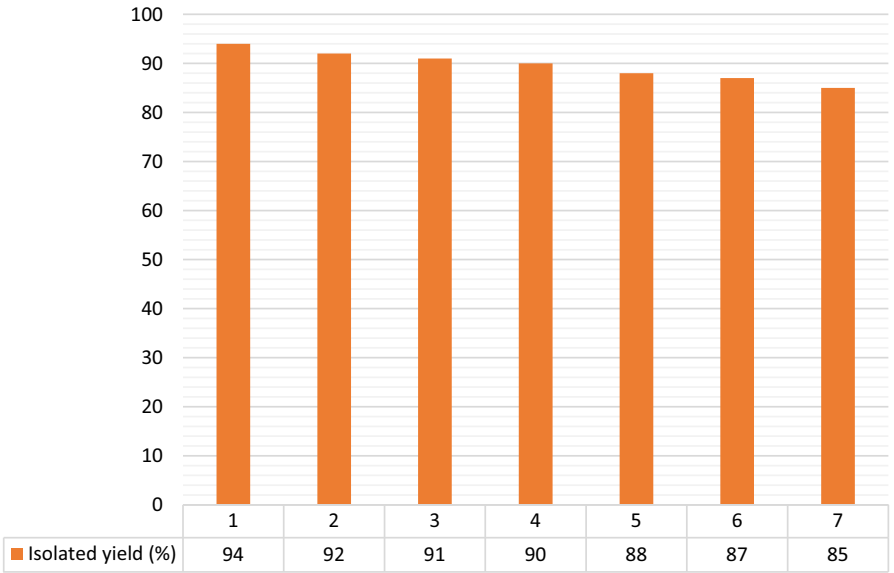


Fig. 5 The recycling experiment of the [nano-MCM-41@$(CH_2)_3$-1-methylimidazole]Br_3 (10 mg) in the trimethylsilylation of benzyl alcohol

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