An efficient, eco-friendly process for aldol and Michael reactions of trimethylsilyl enolate over organic base-functionalized SBA-15 catalysts

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Abstract

1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD, a bicyclic guanidine base) functionalized SBA-15 was found to be an efficient catalyst for aldol reaction of trimethylsilyl enolate with aldehydes. Both aryl aldehydes and alkyl aldehydes provided aldol products in good yields. The applicability of this catalyst was extended to Michael reaction and in the synthesis of quaternary carbon. This novel heterogeneous catalyst offers several attractive advantages over soluble base catalysts such as high catalyst activity under mild reaction condition, easy recovery and reusability of the catalyst.
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1. Introduction

Numerous efforts have been made in the recent years for the development of environmentally benign solid catalysts for clean process in fine chemical synthesis [1]. Aldol reaction is one of the most fundamental and important C–C bond forming reactions [2]. The most prominent development in this reaction is the use of enoxysilane as enolate, developed by Mukaiyama [3]. The Mukaiyama reaction is classically catalyzed by a Lewis acid, which initiates the enoxysilane addition through the electrophilic activation of the aldehyde. Alternatively, the enolate can also be activated through nucleophilic cleavage of the O–Si bond or via Lewis base coordination to the silicon atom. Denmark et al. focused on the alternative approach by reacting more electropositive trichlorosilylenol ether in the presence of phosphorane [4] or a more strained silacyclobutylketene acetal [5]. This concept was employed to commercially available and more stable trimethylsilyl or dimethylsilyl enolate in the presence of a Lewis base such as dimethylsulfoxide [6], phosphine oxide [7] or chloride ion [8] to activate the silylenolate as a hypervalent silicate intermediate. Mukaiyama aldol reactions of silyl enol ether and aldehyde are promoted by a variety of Lewis

acids such as TiCl$_4$, SnCl$_4$, ZnCl$_2$, etc., using either stoichiometric or catalytic amount under homogeneous condition [9]. Several heterogeneous Lewis acid catalysts such as Nafion-H, montmorillonite clay, SiO$_2$–Al$_2$O$_3$, sulfated zirconia and titanosilicates have been reported [10]. Various homogeneous Lewis bases are also reported to catalyze this reaction [6–8,11]. In the present study focus has been given to catalyze aldol reaction of trimethylsilyl enoaltes in the presence of heterogeneous Lewis base catalysts (Scheme 1).

The goals of this study were (1) to design a suitable heterogeneous base catalyst, (ii) to compare the catalytic efficiency of the homogeneous and heterogeneous catalysts and (iii) to apply the present catalytic system for the synthesis of a variety of β-hydroxy methyl esters.

2. Experimental

2.1. Catalysts preparation

2.1.1. Synthesis of SBA-15

Mesoporous silica SBA-15 was synthesized according to the reported procedure [12]. In a typical synthesis, 10 g of amphiphilic triblock copolymer, poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (average molecular weight = 5800, Aldrich Co.), was dispersed in 75 ml of water and 300 ml of 2 M HCl solution while stirring. 21.25 g

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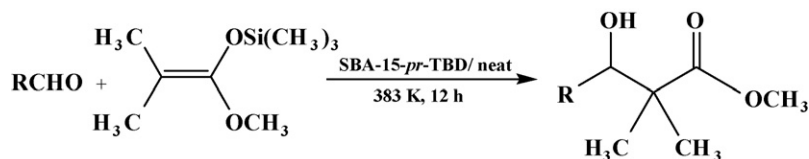
Scheme 1. Aldol condensation reaction of trimethylsilyl enolate with aldehydes.

of tetraethyl orthosilicate (TEOS, Aldrich Co.) was added to it. This gel was continuously stirred at 313 K for 24 h, and finally crystallized in a Teflon-lined autoclave at 373 K for 2 days. After crystallization, the solid product was centrifuged, filtered, washed with deionized water, and dried in air at room temperature. SBA-15 powder was obtained by calcining the materials in air at 823 K for 6 h.

2.1.2. Synthesis of SBA-15-pr-NH₂

In a typical organo-functionalization, SBA-15 was activated under vacuum at 423 K for about 3 h. To it, 3-aminopropyltriethoxysilane (9 mmol per 3 g of SBA-15, Lancaster) in 100 ml of dry toluene was added and refluxed under nitrogen for 6 h. Soxhlet extraction with dichloromethane (12 h) and then with acetone (12 h) yielded NH₂-functionalized SBA-15 (SBA-15-*pr*-NH₂) materials [13,14].

2.1.3. Synthesis of SBA-15-pr-TBD

SBA-15 was activated under vacuum at 423 K for about 3 h. To it, 3-chloropropyltriethoxysilane (9 mmol per 3 g of SBA-15, Lancaster) in 100 ml of dry toluene was added and refluxed under nitrogen for 6 h. Soxhlet extraction with dichloromethane (12 h) and then with acetone (12 h) yielded Cl-functionalized SBA-15 (SBA-15-*pr*-Cl) materials.

TBD (2.5 mmol, Aldrich Co.) was taken in 30 ml of dry chloroform and stirred for 30 min under nitrogen environment at reflux condition. Then, 1 g of SBA-15-*pr*-Cl was added and stirring was continued for 12 h. Soxhlet extraction with CHCl₃ (10 h) and then with CH₃COCH₃ (12 h) yielded SBA-15-*pr*-TBD catalyst.

2.1.4. Synthesis of SBA-15-pr-Im

Imidazole (2.5 mmol, Aldrich Co.) was taken in 30 ml of dry chloroform and stirred for 30 min under nitrogen environment at reflux condition for complete dissolution. Then, 1 g of SBA-15-*pr*-Cl was added and stirring was continued for 12 h. Soxhlet extraction with CHCl₃ (for 10 h) and then with CH₃COCH₃ (for 12 h) yielded SBA-15-*pr*-Im [14].

2.2. Catalyst characterization

X-ray diffractograms were recorded on Rigaku Multiplex diffractometer using Cu Kα radiation and a proportional counter as detector. A divergence slit of 1/328 on the primary optics and an anti-scatter slit of 1/168 on the secondary optics were employed to measure data in the low angle region. Transmission electron micrographs (TEM) of the samples were scanned on a JEOL JEM-3010 microscope operating at 300 kV. The samples for TEM were dispersed in isopropyl alcohol, deposited on

a Cu-grid and dried. The C, H and N composition was determined by a Carlo-Erba 1106 analyzer. The specific surface area (BET) of the samples was determined using a Micromeritics ASAP 2010 volumetric adsorption analyzer. Before N₂ adsorption organobase-functionalized SBA-15 samples were evacuated in vacuum at 373 K. The data points of p/p_0 in the range of about 0.05–0.3 were used in the calculations. The micropore volume was estimated from the *t*-plot and the pore diameter was estimated using the Barret–Joyner–Halenda (BJH) model. FT-IR spectra were recorded on a Shimadzu 8201 PC spectrophotometer in the region 400–4000 cm⁻¹.

2.3. General reaction procedure

Heterogeneous catalysts were activated in vacuum at 373 K for 1 h before reaction. A mixture of aldehyde (3 mmol), 1-methoxy-2-methyl-1-trimethylsilyloxypropene (6 mmol) and catalysts (0.3 mmol) were stirred at 383 K for 12 h. After the reaction, catalysts were separated by simple filtration and washed thoroughly with diethyl ether. Eight millilitre of 1 M aqueous HCl was added to the reaction system. After stirring vigorously for a while, the product was extracted with diethyl ether (15–20 mL). The combined organic phases were washed with brine and dried over anhydrous Na₂SO₄. The solution was concentrated in vacuum followed by the purification using flash silica gel chromatography to give desired products. Progress of the reaction was monitored with Shimadzu GC (equipped with a flame ionization detector and a packed column with 10% SE-30). Products were identified with GC–MS and ¹H NMR.

3. Results and discussion

3.1. Catalysts characterizations

In order to functionalize the organic catalysts, bases such as primary amine, imidazole and TBD were tethered to the surface of siliceous SBA-15 through the propyl-spacer. Organic base-functionalized SBA-15 molecular sieves were prepared by the secondary synthesis route using the protocol shown in Scheme 2. In the first step, SBA-15-*pr*-Cl was prepared by silylation/condensation of vacuum-dried SBA-15 with 3-chloropropyltriethoxysilane, which was then, in the second step, react with TBD or imidazole to form TBD-functionalized SBA-15 (SBA-15-*pr*-TBD) and imidazole functionalized SBA-15 (SBA-15-*pr*-Im) materials. Chemical analysis (Table 1) revealed that SBA-15-*pr*-Cl contained 2.31 mmol of –*pr*-Cl groups per gram silica. Out of this, 1.5–1.8 mmol was participated in reaction with bases (Table 1).
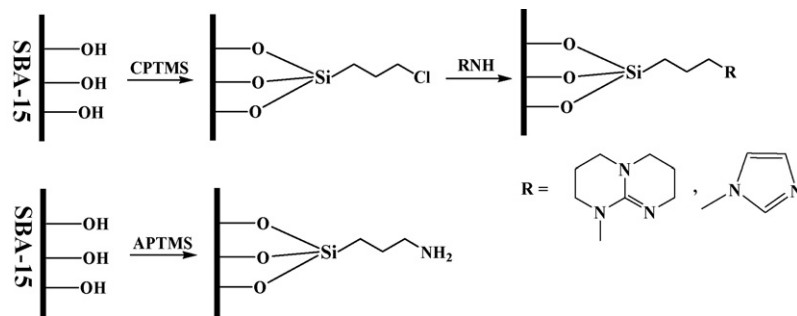
Scheme 2. Procedure for functionalization of organic bases on SBA-15 surface.

Table 1
Physicochemical properties of SBA-15 and organo-functionalized SBA-15 materials

Material	Organic amine (mmol/g material)[a]	Elemental analysis (wt%)			XRD analysis		S_{BET} (m^2/g)	Pore volume (cm^3/g)			Pore diameter (nm)[b]	Wall thick-ness (nm)
		C	H	N	d_{100} (nm)	Unit cell parameter (nm)		Total	Mesopore	Micropore		
SBA-15	–	0.5	1.5	0	9.8	11.3	961	1.65	1.53	0.12	7.3 (7.5)	4.0
SBA-15-pr-NH₂	2. 1	9.0	1.6	2.9	10.0	11.5	743	1.43	1.30	0.13	7.0	4.5
SBA-15-pr-Im	1.8	11.1	1.3	5.0	10.0	11.5	631	1.17	1.06	0.11	6.9	4.6
SBA-15-pr-TBD	1.5	10.5	1.3	6.3	9.9	11.4	587	1.00	0.92	0.08	6.6 (7.0)	4.7

[a] Values estimated from C, H and N analysis.
[b] Values in parentheses are those estimated from TEM.

Fig. 1 shows the XRD profiles of SBA-15 and organo base functionalized SBA-15 materials. All the samples showed very similar XRD patterns. The samples showed three well-resolved diffraction peaks due to (1 0 0), (1 1 0) and (2 0 0) reflection in the 2θ range of 0.8–2°, that could be indexed according to a 2D
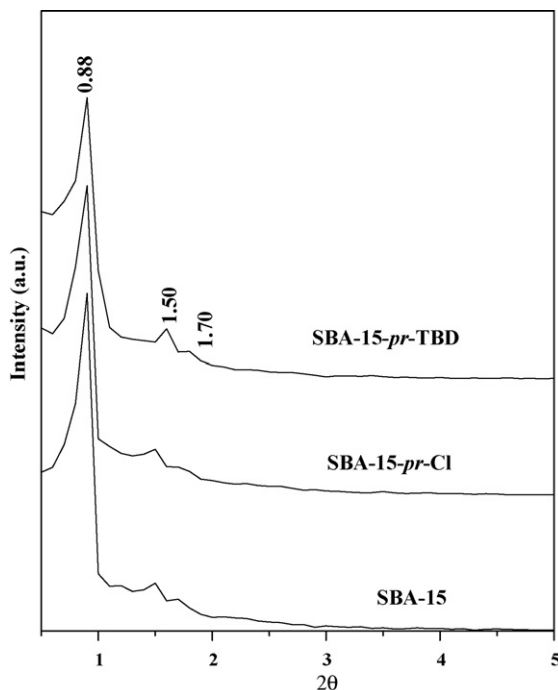

Fig. 1. XRD profiles of SBA-15 and organo-functionalized SBA-15 materials.

hexagonal *p6mm* symmetry [12]. Organic base incorporation did not alter the long-range ordering of the mesoporous structure. Inter-planar spacing (d_{100}) and unit cell parameter (a_0) of various functionalized SBA-15 materials are listed in Table 1. The d-spacing (d_{100}), estimated from the position of the low-angle peak is in the range of 9.8 to 10.4 nm. The unit cell parameter calculated using the equation $a = 2d_{100}/\sqrt{3}(11.3 - 11.9)$ nm (Table 1) is in good agreement with the values reported by others [12].

The nitrogen adsorption/desorption isotherms of SBA-15 and TBD-functionalized SBA-15 samples are of type IV nature (Fig. 2) and exhibit a H1 hysteresis loop, which is typical of mesoporous solids [14]. Furthermore, the adsorption branch of each isotherm showed a sharp inflection at a relative pressure value of about 0.68. This is characteristic of capillary condensation within uniform pores. The position of the inflection point indicates mesopore structure, and the sharpness of these steps indicates the uniformity of the mesopore size distribution. A good match between the points of inflection on the adsorption branch of both isotherms suggests that samples have similar pore sizes (~6.6 nm) (Fig. 2). The low mesopore volume was observed in case of TBD-functionalized SBA-15 because the mesopores were partially blocked by functionalized organic base (Table 1).

TEM studies established the 2D hexagonal pore arrays and mesostructure of SBA-15 materials (Fig. 3). The pore diameter estimated form the TEM measurements (~7.50 nm) agrees well with that obtained (7.3 nm and 6.6 nm) from nitrogen adsorption (BJH) method for SBA-15 and SBA-15-pr-TBD samples. The samples investigated in the present study show a curved
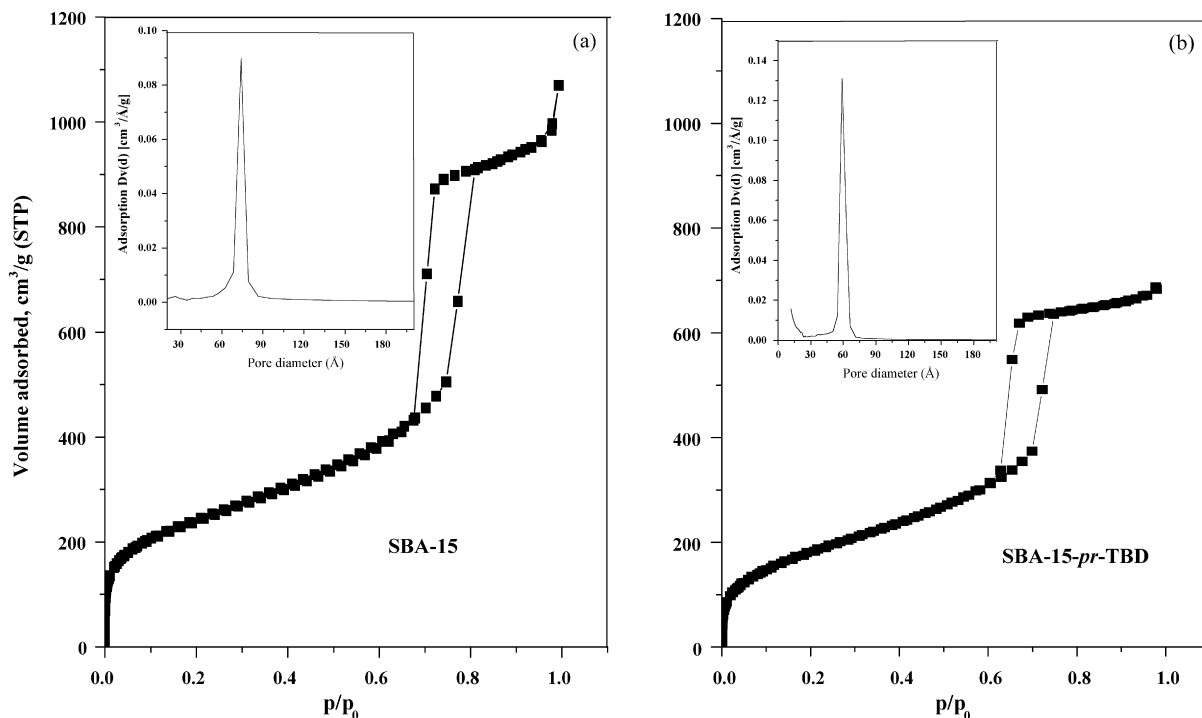
Fig. 2. Nitrogen adsorption–desorption isotherms of (a) SBA-15 and (b) SBA-15-*pr*-TBD. Inset shows the pore size distribution.

arrangement of the channels in the mesoscopic range consistent with the high TEOS to template (EO_{20}–PO_{70}–EO_{20}) ratio in the samples during their synthesis.

FT-IR spectroscopy also provided evidence for organo-functionalization. In case of SBA-15-*pr*-NH_2, the IR peaks at 3325 and 3300 cm^{-1} were observed. These peaks were probably due to the N–H stretching modes of the functionalized-propyl amine. In the case of imidazole and TBD functionalized SBA-15, no peak was observed due to N–H stretching. This may be due to the hydrogen of secondary NH is used-up during anchoring covalently to the SBA-15 surface. Characteristic peaks due to C–H stretching vibrations (of propyl spacer and cycloalkane ring) were appeared in the range of 2800–2950 cm^{-1} and skeleton vibration of imidazole and TBD ring were observed in the
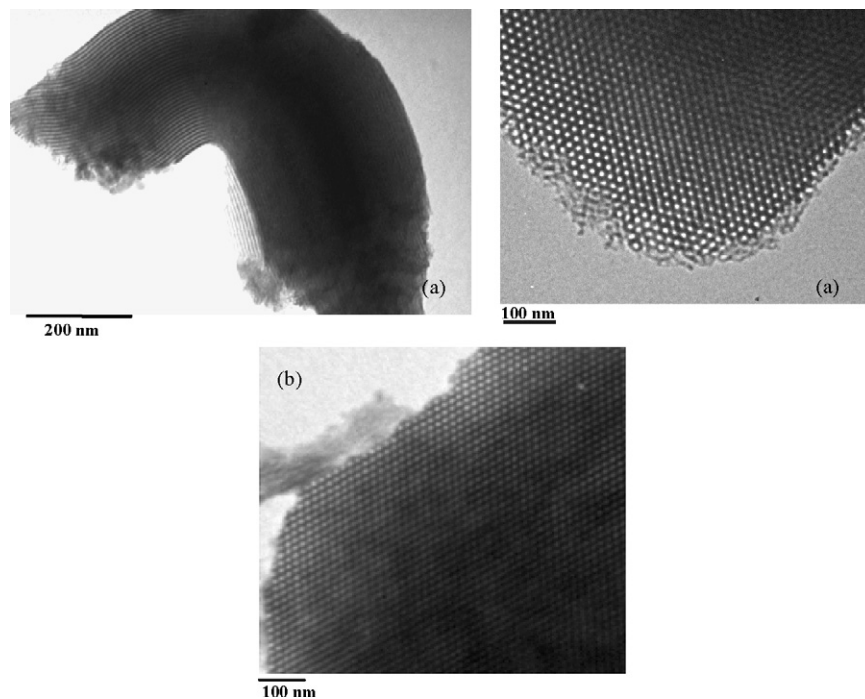

Fig. 3. TEM images of (a) SBA-15 and (b) SBA-15-*pr*-TBD.

Table 2

Homogeneous Lewis base catalyzed aldol condensation of benzaldehyde and 1-methoxy-2-methyl-1-trimethylsiloxypropene

Entry no.	Amines	pK_a[a]	Yield (%)
1	None	–	0
2	Pyridine *N*-oxide	–	36
3	Pyridine	5.2	27
4	*N,N*-Dimethylaminopyridine	9.7	45
5	Imidazole	7.0	39
6	*N*-Methylimidazole	–	48
7	1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD)	–	53
8	7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD)	13.0	65
9	1,8-Diazabicyclo[5.4.0]undec-7ene (DBU)	11.9	60

Reaction conditions: 1-methoxy-2-methyl-1-trimethylsiloxypropene (6 mmol), benzaldehyde (3 mmol), catalysts (0.3 mmol), reaction temperature (383 K), run time (12 h).

[a] pK_a values for the aqueous solution of the corresponding conjugate acids.

range of 1400–1650 cm^{-1}. It should be noted that these peaks were absent in non-functionalized SBA materials. TBD and imidazole bases could not be deposited directly by impregnation on the unsilynated SBA-15 surface as it was leached out during Soxhlet extraction with solvents. In this case, the IR spectrum of the solid after the extraction did not detect adsorbed TBD. In other words, in the absence of –Cl groups of the 3-chloropropyltriethoxysilane, the organic bases could not be anchored. The –NH group of TBD and imidazole reacts with the –Cl forming N–C bonds and eliminating HCl in the process.

3.2. Catalytic activity

In the first series of experiments, various homogeneous bases such as pyridine-*N*-oxide, *N,N* dimethylaminopyridine, *N*-methylimidazole, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 7-methyl TBD (MTBD), 1,8-diazabicyclo[5.4.0]undec-7ene (DBU) were investigated for aldol reaction of trimethylsilyl enolate with benzaldehyde in the solvent-free condition and the results are summarized in Table 2. There was a trend that the

reaction with the strong base having large pK_a value [15] offer better yields. Hence, MTBD was found to be the best catalyst among the above-mentioned homogeneous Lewis base catalysts.

Table 3 presents the results of the aldol condensation of benzaldehyde and 1-methoxy-2-methyl-1-trimethylsiloxypropene over various heterogeneous Lewis base functionalized SBA-15 catalysts. The reaction of benzaldehyde in the presence of catalytic amount of the base immobilized catalysts gave products with moderate to high yields (Table 3, entries 2–4). The activity of base-free SBA-15 silica was very low (2% yield), confirming that anchored bases were the catalytic species of immobilized catalysts. The activity was strongly dependent on the type of base anchored to the support. The activity of the three bases is in the order, SBA-15-*pr*-NH$_2$ < SBA-15-*pr*-Im < SBA-15-*pr*-TBD (Table 3, entries 2–4). It should be noted that organic base anchored catalysts exhibited higher activity than conventional solid bases such as MgO and hydrotalcite (Table 3, entries 8 and 9) [16]. The reactions were also performed in various organic solvents as shown in Table 3. Nitrogen containing solvents such as *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMA) were found to be the superior

Table 3

Heterogeneous Lewis base catalyzed aldol condensation of benzaldehyde and 1-methoxy-2-methyl-1-trimethylsiloxypropene

Entry no.	Catalysts	Solvent	Yield (%)
1	SBA-15	None	2
2	SBA-15-*pr*-NH$_2$	None	18
3	SBA-15-*pr*-Im	None	51
4	SBA-15-*pr*-TBD	None	70
5	SBA-15-*pr*-TBD (recycle-1)	None	72
6	SBA-15-*pr*-TBD (recycle-2)	None	68
7	SBA-15-*pr*-TBD (recycle-3)	None	68
8	MgO[a]	None	19
9	Mg–Al hydrotalcite (1:1)[a]	None	15
10	SBA-15-*pr*-TBD	Methanol[b]	4
11	SBA-15-*pr*-TBD	Tetrahydrofuran[b]	47
12	SBA-15-*pr*-TBD	Acetonitrile[b]	49
13	SBA-15-*pr*-TBD	*N,N*-Dimethylformamide	63
14	SBA-15-*pr*-TBD	*N,N*-Dimethylacetamide	67

Reaction conditions: 1-methoxy-2-methyl-1-trimethylsiloxypropene (6 mmol), benzaldehyde (3 mmol), catalysts (0.3 mmol), reaction temperature (383 K), run time (12 h).

[a] MgO and Mg–Al (1:1) hydrotalcite were prepared as per the reported procedure.

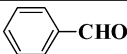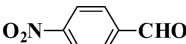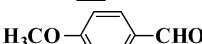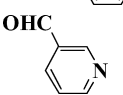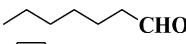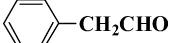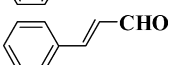[b] Reactions were performed at their reflux temperature.

solvent. However, the reaction proceeds equally well without using these solvents.

To investigate the leaching phenomena of any catalytic active species in solution, a model reaction was examined for aldol condensation of benzaldehyde and 1-methoxy-2-methyl-1-trimethylsiloxypropene over SBA-15-*pr*-TBD catalyst. When the solid catalyst was removed at an early stage of the reaction ($t = 2$ h, 18% yield), the reaction did not proceed further. This result confirms heterogeneous catalytic activity of SBA-15-*pr*-TBD and no contribution from homogenous catalysis. Catalyst was easily separated from the reaction mixture by simple filtration and reused. The recovered catalyst was washed thoroughly with diethyl ether and acetone, and dried at 373 K for 2 h and reused in several recycling experiments. Similar catalytic activity was observed even after three recycles (Table 3, entries 5–7).

Representative examples of the aldol condensation of several aldehydes to 1-methoxy-2-methyl-1-trimethylsiloxypropene over SBA-15-*pr*-TBD catalyst are summarized in Table 4. In all the cases, the reaction proceeded smoothly in the presence of a catalytic amount of SBA-15-*pr*-TBD to afford β-hydroxy methyl esters in high yields. Electron donating group in the aromatic ring such as –CH₃ group accelerate the reaction rate while electron withdrawing group such as –NO₂ retard the reaction rate. Aldehydes having highly coordinating groups

Table 4
SBA-15-*pr*-TBD catalyzed aldol condensation of 1-methoxy-2-methyl-1-trimethylsiloxypropene with a variety of aldehydes

Entry no.	Aldehydes	Yield (%)
1	C_6H_5–CHO	70
2	H_3C–C_6H_4–CHO	81
3	O_2N–C_6H_4–CHO	58
4	H_3CO–C_6H_4–CHO	57
5	OHC–pyridine	47
6	$CH_3(CH_2)_4$CHO	62 (12)[a]
7	C_6H_5–CH₂CHO	60 (10)[a]
8	C_6H_5–CH=CH–CHO	85

Reaction conditions: 1-methoxy-2-methyl-1-trimethylsiloxypropene (6 mmol), aldehyde (3 mmol), catalysts (0.3 mmol), reaction temperature (383 K), run time (12 h).

[a] Values in parenthesis represents the percentage yield of self-condensed product.

Table 5
SBA-15-*pr*-TBD catalyzed Michael reaction of enones with 1-methoxy-2-methyl-1-trimethylsiloxypropene under solvent free condition
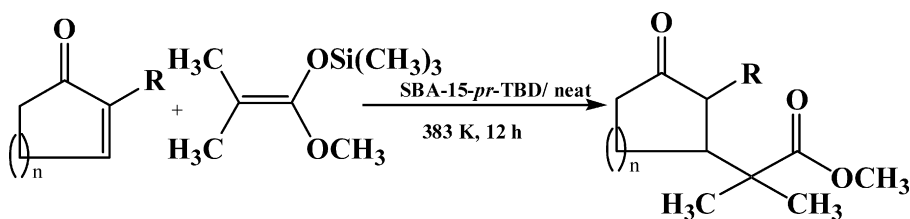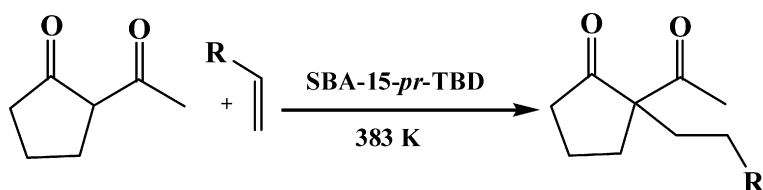

Entry no.	R	n	Yield (%)[a]
1	H	1	75
2	CH₃	1	70[a]
3	H	2	78
4	CH₃	2	72[a]

Reaction conditions: 1-methoxy-2-methyl-1-trimethylsiloxypropene (6 mmol), enones (3 mmol), catalysts (0.3 mmol), reaction temperature (383 K), run time (12 h).

[a] Diasteroselectivity was not determined.

Table 6
SBA-15-*pr*-TBD catalyzed Michael reaction of 2-acetylcyclopentanone with alkenes

Entry no.	R	Time	Yield (%)
1	CN	12	70
2	COOCH₃	8	87
3	COOC₂H₅	8	88
4	COOC₆H₅	8	92

Reaction conditions: 2-acetylcyclopentanone (3 mmol), alkenes (6 mmol), catalysts (0.3 mmol), reaction temperature (383 K).

such as pyridyl group (Table 4, entry 5) provided successfully the desired product in moderate yield. When the reaction was carried out with aliphatic aldehydes (Table 4, entry 6), self-condensed aldol adduct was also observed along with the aldol product. The aldol reaction might proceed via the activation of trimehtylsilyl enol ether by forming a hypervalent silicate between nitrogen atom of TBD and silicon atom of the enolate.

Several heterogeneous catalysts are reported for Michael addition reaction [17]. To see the versatility of this catalyst, the study was extended to Michael reaction involving α,β-unsaturated carbonyl compounds. As shown in Table 5, the reaction proceeded smoothly for a variety of substrate under solvent free condition using SBA-15-*pr*-TBD catalyst. In the present study, diastereoselectivity was not determined for the Michael products (Table 5, entries 2 and 4).

One-step synthesis of a quaternary carbon is a difficult task [18]. Using this catalytic methodology, quaternary carbon was synthesized by reacting 2-acetylcyclopentanone with suitable acceptors. Various activated terminal alkenes, for example acrylonitrile (Table 6, entry 1) and acrylates (Table 6, entries 2–4), were tested as suitable acceptors.

4. Conclusion

In summary, an efficient and environmental friendly catalyst was developed for aldol and Michael reaction under solvent free condition. This methodology can be applied to wide range of substrates making it a useful addition to the organic chemists. These reactions are easy to perform and the purification protocol is simple. TBD is inexpensive and commercially available, and the heterogenised TBD catalyst can be easily filtered and reused for several cycles. Apart from the experimental simplicity, the advantage of this methodology is the use of cheaper, milder and efficient catalysts for various C–C coupling reactions, makes it an interesting candidate for commercial exploitation.

Acknowledgements

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