Transesterification of β-keto esters catalysed by basic porous material *

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β-keto esters have been successfully transesterified with primary, secondary, tertiary, allylic and alkynic alcohols in good yields using TBD anchored on MCM support for the first time. The hybrid solid base catalyst can be recycled several times with consistent activity.

KEY WORDS: transesterification; β-keto esters; TBD-MCM; reusability

1. Introduction

Transesterification is an important organic transformation wherein an ester is transformed into another through interchange of the alkoxy moiety. Transesterification is a preferred process to the esterification of carboxylic acids of low solubility with alcohols because esters, which are the starting materials for transesterification are commonly soluble in most of the solvents.

Typical transesterification is catalysed by strong acids [1] such as hydrochloric, phosphoric, sulphuric, *p*-toluenesulphonic acid, soluble base catalysts, metal alkoxides [2], carbonates [3] and enzymes [4]. The reaction employing acids and bases is incompatible to the modern synthetic industrial chemistry that desires to be highly efficient, selective, ecofriendly and preferably catalytic. Consequently, evolution of titanium(IV) alkoxides [5] and alkyldistannoxanes [6], homogeneous catalysts and kaolinite [7], zeolites [8] and alumina oxides [9], heterogeneous catalysts for transesterification of β-keto esters reflects the current status of research in this area. These catalysts possess inherent disadvantages that limited the scope of their utility in the transesterification reactions such as (1) tedious preparation of the catalysts and (2) confinement of the utility to certain type of esters only.

Attention is focussed recently on the development of solid bases, which are scarcely used compared to solid acids so far to effect the transesterification. Solid bases such as hydrotalcites [10] and guanidine heterogenised on polymer [11] are used for the transesterification reactions.

The recently developed family of mesoporous materials [12] with their tunable large pore sizes displayed the exposition of the inherently present acid [13] and base catalytic properties [14] will find and enlarge their spectrum of applications as novel catalysts in fine chemical synthesis. Brunel *et al.* [15] were the first to report the covalent attachment of organo-amino groups on MCM-41. The modified mesoporous material/silica anchored with organic basic moieties are found to be excellent catalysts for Knoevenagel, aldol, and Michael reactions [15–18].

Herein, we report the transesterification of the β-keto esters for the first time using a heterogeneous strongly basic catalyst 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) anchored on MCM-41 (scheme 1). The TBD-MCM consists of a guanidine base, which is covalently coupled to an inorganic siliceous mesoporous material support with a wide scope of utility. 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) is the prototype for a group of strong guanidine bases which can be used as stoichiometric reagents or as catalysts. The pK_b values of these bases are $\sim$25, ensuring a well-defined and strong basicity [19]. TBD contains a N–H group, which can be immobilized by nucleophilic attack on an immobilized electrophile.

2. Experimental

2.1. Preparation of the catalyst

The TBD-MCM catalyst is prepared in three steps [14] *viz*., the preparation of the mesoporous material (pure silica MCM-41) [20] followed by the reaction of the calcined solid (3 g) with 3-trimethoxy silylpropoxy methyloxirane (4.5 mmol) in dry toluene at reflux for 24 h (EP-MCM). The glycidylated MCM-41 (1 g) is allowed to react with TBD (2.2 mmol) in toluene (15 ml) at 298 K for 10 h, and excess TBD was removed by soxhlet extraction with CH_2Cl_2 (scheme 1). IR, UV-Vis-DRS, solid-state ^{13}C-NMR, BET surface area and thermogravimetric analysis attributed to the covalent bonding of the organic moiety to MCM-41.

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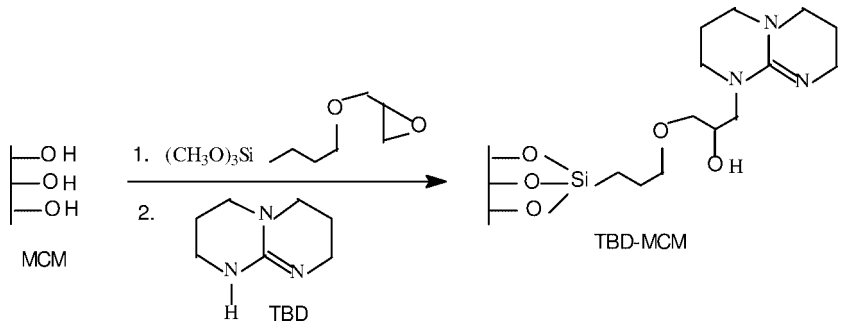


Scheme 1.

2.2. Characterisation

TG-MS investigations are carried out by means of a Mettler Toledo TGA apparatus coupled with a Balzers Thermostar™ GSD 300T Thermo-Cube type mass spectrometer. Samples of few milligrams are heated in nitrogen atmosphere at a rate of 25 °C/min.

UV-Vis-DRS and FTIR spectrometry are performed on samples pressed into pellets as KBr disks using a GBC Cintra 10e spectrometer and Bio-Rad FTS-175 spectrometer, respectively.

^{13}C-NMR spectra are performed on a Unity (400 MHz) NMR spectrometer. Surface area experiments are carried out on AutoChem 2910, Micromeritics, USA.

Proton nuclear magnetic resonance (^{1}H NMR) spectra are taken on a Gemini Varian (200 MHz) spectrometer (using TMS as an internal standard). Mass spectroscopic analyses are performed with a micromass VG 7070H spectrometer.

3. Catalytic reactions

3.1. Typical procedure

In a typical experimental procedure, the catalyst (0.2 g) is suspended in dry toluene (10 ml) followed by the addition of a mixture of methyl acetoacetate (1 mmol, 0.108 ml), 1-butanol (2 mmol, 0.182 ml) and the mixture is stirred at 100 °C in a two-necked round bottom flask. The reaction was monitored by TLC. After completion of the reaction, the catalyst was filtered and used for recycling experiments. The filtrate was concentrated and purified by column chromatography (hexane/ethylacetate, 95/5 v/v) to afford *n*-butyl acetoacetate (table 1, entry 2) as viscous colourless liquid, yield: 0.126 g (80%). ^{1}H NMR: δ 0.8–0.9 (t, 3H), 1.2–1.4 (m, 2H), 1.45–1.65 (m, 2H), 2.15 (s, 3H), 3.35 (s, 2H), 4–4.1 (t, 2H).

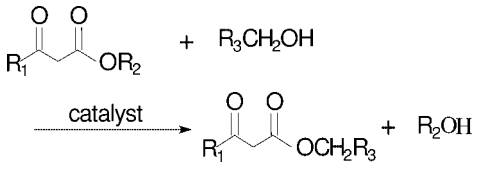
3.2. Recycling of the catalyst

After completion of the reaction, the catalyst is filtered, washed thoroughly with toluene, dried under vacuum and used for the transesterification reaction following the procedure as described above.

Table 1
Transesterification of β-keto esters catalysed by TBD-MCM.

S.No	Substrate		Alcohol	Time	Yield[a]
	R_1	R_2	R_3	(h)	(%)
1	CH_3	CH_3	Benzyl	24	60
2	CH_3	CH_3	Butyl	24	80 (75[b])
3	CH_3	C_2H_5	Butyl	12	100
4	CH_3	CH_3	1-hexyl	12	80
5	CH_3	CH_3	1-octyl	6	52
				24	25[c]
				24	25[d]
6	CH_3	CH_3	Geranyl	24	83
7	CH_3	C_2H_5	Methyl	12	45
8	CH_3	CH_3	2-amino 1-phenyl ethyl	12	60
9	CH_3	CH_3	Propargyl	24	45

[a] Yields based on ^{1}H NMR, based on β-keto ester.
[b] 5th recycle.
[c] Using homogeneous catalyst.
[d] Blank reaction.



Scheme 2.

4. Results and discussion

The samples of mesoporous material Cal. MCM-41 and TBD-MCM were subjected to TG-SDTA measurements. The decomposition behaviour of free MCM-41 and the loaded MCM-41 (TBD-MCM) has been compared to understand the type and site of the linkage of the organo-amine with MCM-41. The total loss of organic moiety as revealed in the thermogram from 286 to 710 °C accounts to 21.8% which is approximately equivalent to the loss of organic moiety, *i.e.*, 0.58 mmol/g present in TBD-MCM [12].

The organic coverage of the modified material was confirmed by TG-mass, wherein the fragments of the TBD present in MCM were detected. TG-MS of pure TBD was compared with grafted one. Pure TBD decomposed from 140 to 230 °C, whereas TBD-MCM shows loss from 240 to 680 °C. In both cases, the same fragments such as NH_2, CH_2^+, $C_3H_6^+$ and CO_2 were found by which it could be con-

firmed that TBD anchored without any change and formed a covalent bond with MCM-41. The BET surface areas and pore volumes of pure MCM and TBD-MCM were found to be 755, 263 m^2/gm and 1.62, 1.2 ml N_2 STP (standard temperature and pressure), respectively. Therefore, the significant reduction in the surface areas and pore volumes were attributed to the TBD anchored to the inner walls of MCM-41 predominantly [21].

^{13}C-NMR spectroscopy allows the determination of the structure of the grafted organic moiety. The ^{13}C-NMR spectrum of the solid state anchored TBD group attached to MCM was similar to the spectrum of TBD material in $CDCl_3$, except for broadening of the peaks in the solid state.

The UV-visible spectrum of pure TBD which shows λ_{max} 226 nm is shifted to 217 nm on anchoring on the support (TBD-MCM) which indicates an interaction of chromophore on the support silanols. FT-IR spectra of pure TBD and TBD-MCM show the same bands at 805, 1521, 1600, 2414 and 3830 cm^{-1}.

We report in this letter the transesterification of the β-keto esters with a wide scope of utility, possible with varied primary, secondary, tertiary, allyl and alkynic alcohols catalysed by TBD-MCM to realise reusability of the catalyst by filtration to afford good yields. The reactions are in general very clean and no by-products have been observed.

This method is found to be applicable for a wide range of compounds (table 1) and offers distinct advantages over the existing methods. The salient features of this methodology are summed up:

(1) Aliphatic and aromatic esters are successfully transformed into synthetically useful esters. (2) Unsaturated alcohols such as propargyl underwent transesterification affording esters (entry 9). (3) The superiority of our method is demonstrated by the fact that even tertiary butyl esters (entries 2, 3) were prepared using TBD-MCM. Aryl alcohols (entries 1, 8) and the long chain primary alcohols underwent transesterification affording the corresponding esters of commercial use (entry 5) in good yields. Our catalyst can be reused for number of cycles with consistent activity whereas the guanidine heterogenized on polymer is used for nine catalytic cycles only with gradual decrease in base capacity and a parallel loss of catalytic activity of the polymer. This loss of base capacity is explained by an attack of methoxide on the benzylic CH_2 groups, causing leaching of guanidine from the polymer. To overcome this problem, we have chosen a simple alkyl spacer for anchoring of guanidine. Our catalyst is robust and no leaching was observed. These results prove that it is feasible to introduce strong, non-hydroxide basicity into a MCM-41 structure by the covalent bonding of the active centers on MCM carriers. The mechanical stability of the inorganic support materials ensures easy separation of the solid catalyst. The coupling procedure itself is highly convenient, and much more simple and eco-economic. The success of our catalyst lies in the method of immobilization.

In conclusion, we have demonstrated that TBD-MCM acts as an efficient, convenient and reusable catalyst to effect transesterification. The superiority and flexibility of our method over the existing methods coupled with the ease of operation and the simplicity in the work-up involving mere filtration of the catalyst and recyclability should find widespread application in the transesterification of many β-keto esters.

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