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One-pot synthesis of conjugated nitroalkenes by diamino-functionalised mesoporous material

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Nitroalkenes are synthesised for the first time in a one-pot liquid-phase procedure from carbonyl compounds and nitroalkanes using organic-diamine-functionalised mesoporous material (MCM-41) as the catalyst. The yields are reasonable to excellent and the reaction conditions are mild. The hybrid solid base catalyst can be recycled several times with consistent activity.

Keywords: nitroalkenes, mesoporous material, MCM-41, reusability, conversion

1. Introduction

Many ubiquitous organic reactions such as condensations, isomerisations, additions, alkylations and cyclisations essential for production of fine chemicals are coaxed by using soluble bases in stoichiometric amounts, whereas solid base catalysts in place of soluble bases offer an ecofriendly process devoid of environmental problems associated with the salts formed on neutralisation of soluble bases [1–5]. Further these solid base catalysts are tunable, recyclable, easily separable from the liquid reaction mixtures with almost zero emission of effluents.

Nitroalkenes are important precursors for many insecticides [6], fungicides [7] and pharmaceuticals [8]. The preparation of nitroalkenes is generally resorted to by an aldol type C–C bond formation process, in specific Henry condensation of carbonyl compounds with a nitroalkane to β-nitroalcohol followed by dehydration [9].

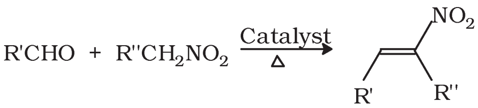
The classical methods provide nitroaldols using soluble bases [10], alkali metal hydroxides, carbonates, bicarbonates, alkoxides, and soluble bases with a surfactant [11], with longer reaction times. Dehydration of nitroalkanols to nitroalkenes effected by several reagents such as methane sulfonylchloride [12], phthalic anhydride [13,14], dicyclohexyl carbodiimide (DCC) [15], pivaloyl chloride [16,17], organic bases, etc. requires high temperatures and longer reaction times. Recently, transition-metal-catalysed aldol reactions to give nitroalkanols were also reported [18]. Ballini et al. attempted [19] sequential synthesis of nitroalkenes starting from aliphatic aldehydes in a solvent free nitroaldol reaction on alumina [20] at room temperature followed by *in situ* dehydration with addition of dichloromethane at 40 °C for 7 h. In view of the disadvantages such as long reaction times [18], expensive and tedious preparation of the catalysts [18], large excess of the nitroalkane and severe reaction conditions, there is a need to develop a mild and efficient base catalyst for the synthesis of nitroalkenes. Preparation of nitroalkenes selectively by one-pot synthesis by an ecofriendly solid catalyst with compatible basicity avoids the formation of polycondensed and Cannizzaro products.

The recently developed family of mesoporous materials [21] with their tunable large pore sizes displayed the exposition of the inherently present acid [22] and base catalytic properties [22,23] will find and enlarge their possible applications as novel catalysts in the fine chemical synthesis. Brunel and his co-workers [24] were the first to report the covalent attachment of organoamino groups on MCM-41. The modified mesoporous materials/silica anchored with organic basic moieties are found to be excellent catalysts for Knoevenagel, aldol and Michael reactions [2,24–26]. Here, we describe the application of newly synthesised diamino-functionalised mesoporous material anchored by 3-trimethoxysilylpropylethylenediamine moiety on calcined MCM-41 [25] for the one-pot synthesis of nitroalkenes in liquid phase under mild reaction conditions at a faster rate for the first time (scheme 1).

2. Experimental

2.1. Preparation of the catalyst

The diamino-functionalised mesoporous catalyst (MPEDA) was prepared in two steps, viz. the preparation of the mesoporous material (pure silica MCM-41) [27] followed by the reaction of the calcined solid (at 550 °C for 6 h) with 3-trimethoxysilylpropylethylenediamine in dry toluene [24] (scheme 2).



Scheme 1.

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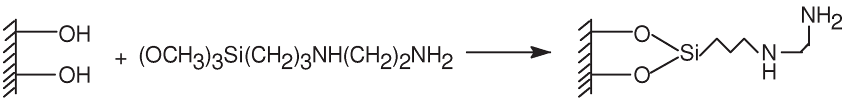


Scheme 2.

2.2. Characterisation

TG-DTA curves were obtained on a Mettler Toledo TG-SDTA apparatus. Samples were heated from room temperature to 1000 °C under nitrogen flow. The sample weight was ca. 10 mg and the heating rate is 10 °C/min.

FTIR spectra of the samples were recorded on a Bio-Rad FTS-175 spectrometer as KBr disks.

The products of the reaction were characterised by NMR, IR, and mass spectroscopic methods. Proton nuclear magnetic resonance (^{1}H NMR) spectra were taken on a Gemini Varian (200 MHz) NMR spectrometer, using TMS as an internal standard. IR spectra were recorded on a Nicolet DX-5 spectrometer. Mass spectroscopic analyses were performed with a Micromass VG 7070H spectrometer.

3. Catalytic reactions

3.1. Typical procedure

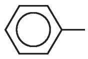
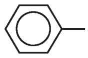
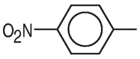
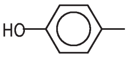
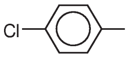
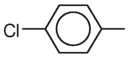
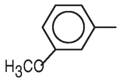
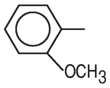
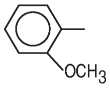
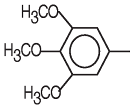
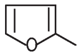
In a typical procedure, 0.2 g catalyst, 141 mg (1 mmol) of p-chlorobenzaldehyde and 0.07 ml (1 mmol) of nitroethane were taken in 10 ml of toluene and heated at 50 °C. The reaction was monitored by TLC. After completion of the reaction, the catalyst was filtered and the filtrate was concentrated to get the desired product. The catalyst was washed with the solvent and reused without any further activation. The product was analysed by ^{1}H NMR, mass and IR. Yield: 187 mg (95%); ^{1}H NMR: δ 2.4 (3 H, s), 7.3–7.5 (4 H, m), 8.0 (1 H, s); IR: ν 1600, 1525 cm^{-1}; MS: $m/z = 197$ (M^+).

3.2. Results and discussion

The nitrogen content of the catalyst is 0.84%. The samples of mesoporous material MCM-41 and diamino-functionalised MCM-41 were subjected to TG-SDTA measurements (figure 1). The decomposition behaviour of the free MCM-41 and the loaded MCM-41 (MPEDA) has been compared to understand the type and site of the linkage of the organoamine with MCM-41. The total loss of organic moiety is indicated in the thermogram from 340 to 852 °C which accounts to 6.8% approximately equivalent to the loss of organic moiety of 0.3 mmol/g present in diamino-functionalised MCM-41.

It is well established that the cationic exchanged amines decompose at less than 600 °C [21]. The thermal stability of organic moiety in MCM-41 in the present case established and revealed by TGA at relatively higher temperatures is attributed to the covalent bonding of the organic moiety to MCM-41. On the other hand, the loss of the amine moiety is revealed through a broad and a sharp endothermic peak at 400–600 and 700–750 °C, respectively.

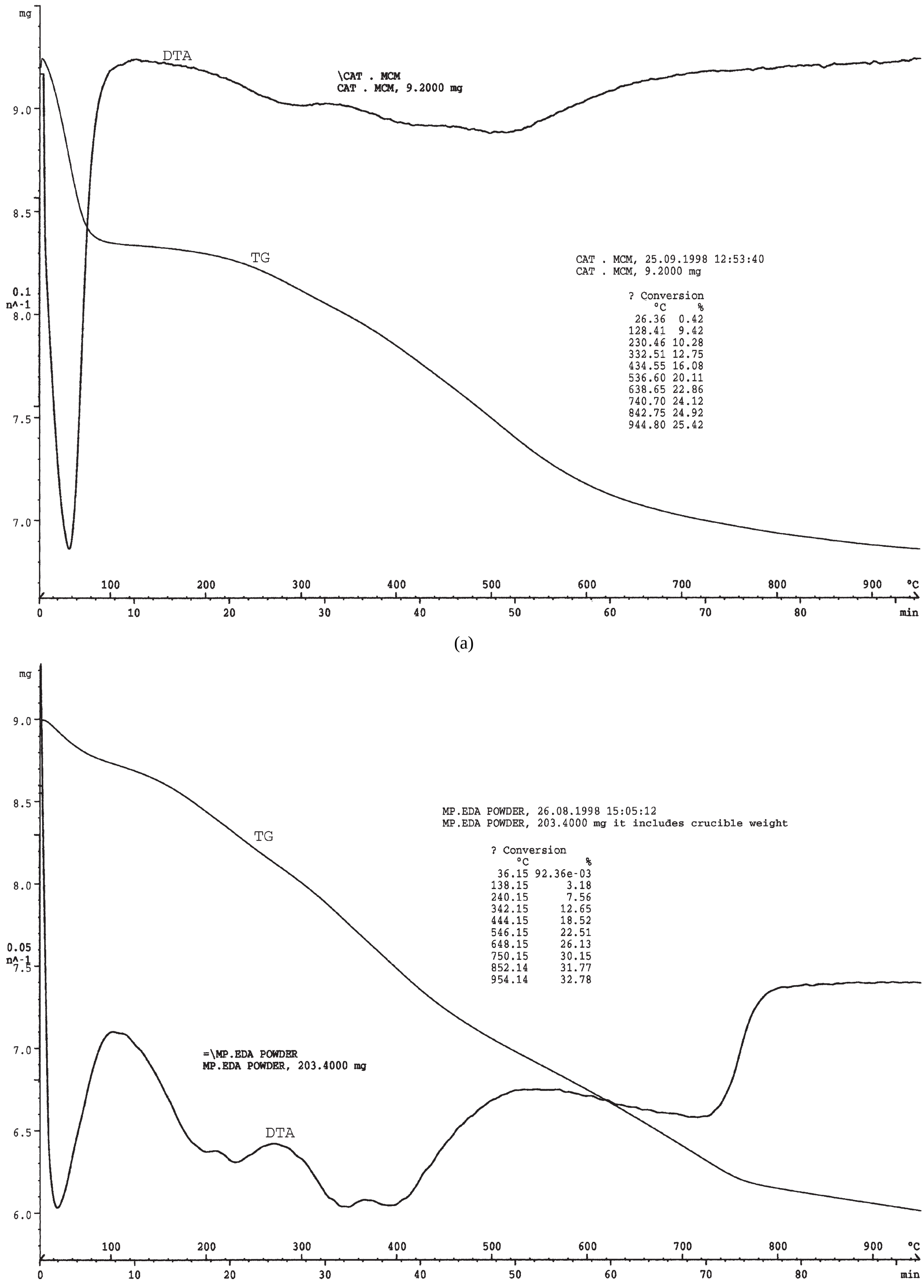
Table 1
Synthesis of conjugated nitroalkenes by diamino-functionalised mesoporous material.

Entry	R′	R″	Time (h)	Yield[a] (%)
1		Me	3	100 (98[b])
2		H	3	97
3		H	3	80 (73.8 : 26.2[c])
4		H	3	74
5		H	3	99 (96[b])
6		Me	3	100
7		H	1	61.5
8		Me	3	100
9		H	1	100 (98[b])
10		H	3	94
11		H	1	92
12	CH_3CH_2	H	2	92 (43.5 : 56.5[c])
13	$(CH_3)_2CHCH_2$	H	2	100 (96[b])

[a] NMR yields based on aldehyde.
[b] 6th recycle.
[c] Aldol product.

In the FTIR, the CH vibration of ethylenediamine appeared between 2700 and 3000 cm^{-1}. The NH_2 group pertaining to ethylenediamine appeared in the range of 1500–1600 and 3100–3200 cm^{-1} [28,29]. The efficacy of this catalyst as a base (0.3 mmol/g of loading) was tested in the synthesis of nitroalkenes (scheme 1). Various aldehydes were reacted with (a) nitromethane and (b) nitroethane as nucleophiles.

With nitromethane as the nucleophile, all the substrates except p-nitrobenzaldehyde and propionaldehyde afforded nitroalkenes exclusively, while with nitroethane all the substrates give only dehydrated products in a single-pot synthesis. All the reactions form the products with high yields. The reusability of the catalyst was checked for several cycles which shows consistent activity.



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CAT . MCM, 25.09.1998 12:53:40
CAT . MCM, 9.2000 mg

        ? Conversion
            °C      %
         26.36   0.42
        128.41   9.42
        230.46  10.28
        332.51  12.75
        434.55  16.08
        536.60  20.11
        638.65  22.86
        740.70  24.12
        842.75  24.92
        944.80  25.42
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(a)

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MP.EDA POWDER, 26.08.1998 15:05:12
MP.EDA POWDER, 203.4000 mg it includes crucible weight

        ? Conversion
            °C         %
         36.15 92.36e-03
        138.15      3.18
        240.15      7.56
        342.15     12.65
        444.15     18.52
        546.15     22.51
        648.15     26.13
        750.15     30.15
        852.14     31.77
        954.14     32.78
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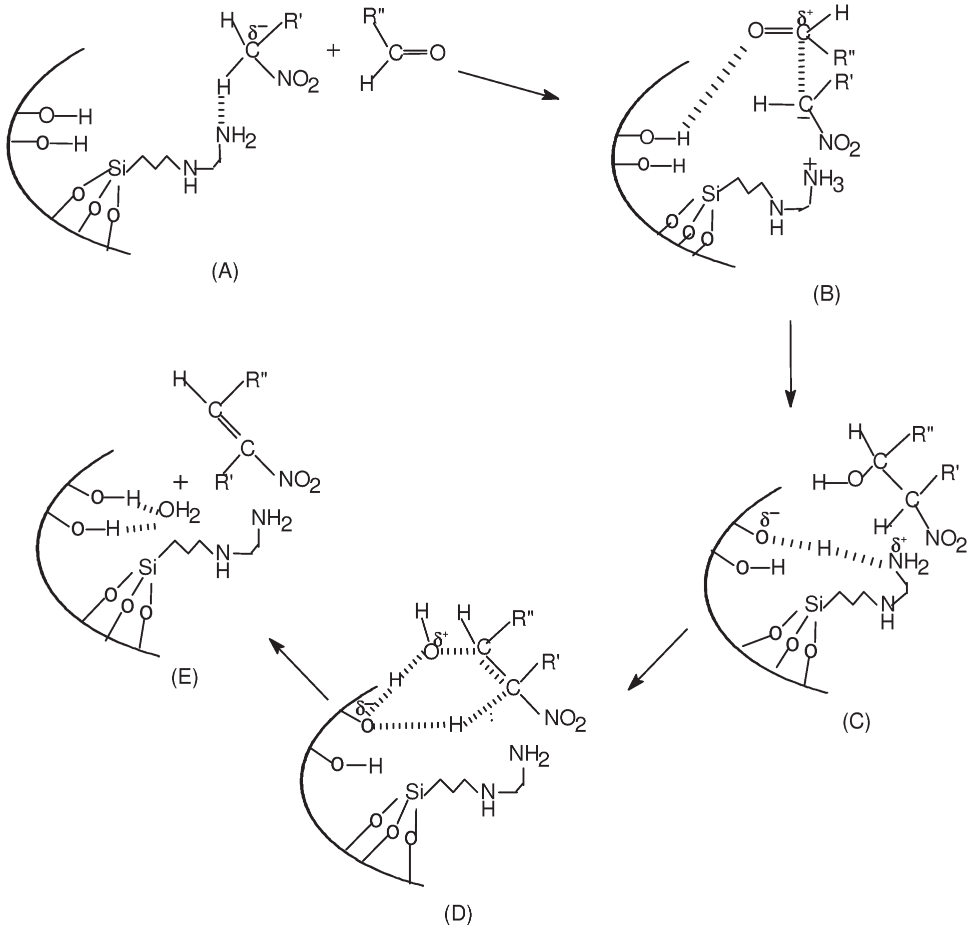
(b)

Figure 1. TG-SDTA results of mesoporous MCM-41 (a) and diamino-functionalised MCM-41 (b).



Scheme 3. Plausible mechanism for nitroalkene synthesis by diamino-functionalised mesoporous material.

A concerted mechanism is proposed in scheme 3 which is similar to that proposed by Angelletti et al. for condensation reactions:

(i) The immobilised primary amino group of the catalyst extracts a proton from the active nitroalkane affording the carbanion.

(ii) The silanol group of the support promotes the nucleophilic addition on the carbonyl compound via a hydrogen bond and restores the free amine thus regenerating the catalyst.

(iii) The nitroaldol promoted by the silanol hydrogen easily dehydrates to afford the nitroalkenes and water thus removed is strongly adsorbed on the hydrophilic matrix surface.

Thus, the solid base developed by us is a possible candidate for commercial exploitation since the reactions are executed at a faster rate under mild conditions in one-pot synthesis to afford nitroalkenes with high yields. Easy preparation of the catalyst and reusability by simple filtration for several cycles with consistent activity and without any further reactivation are additional advantages.

Acknowledgement

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