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Al-MCM-41 as a mild and ecofriendly catalyst for Michael addition of indole to α , β -unsaturated ketones

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1. Introduction

Michael addition and Friedel-Crafts alkylation of heteroaromatics with electron deficient α , β -unsaturated carbonyl compounds constitute powerful methods for direct C-C bond forming reactions extensively used for functionalization of biologically active derivatives with pharmaceutical applications [1–5]. They are also atom efficient and thus are inherently green transformations [6–8]. The development of effective routes to indole architectures has attracted considerable attention as 3-substituted indoles are important building blocks for the synthesis of biologically active compounds and natural products [9-16]. It is well established that regioselectivity in the addition of indoles to electron deficient alkenes is strongly controlled by the reaction medium. Indoles are *N*-alkylated by conjugate addition under alkaline conditions. On the other hand, the formation of C-3 substituted indoles is usually achieved in acid catalyzed addition [17-25]. They are usually carried out in the presence of catalytic and stoichiometric amounts of Lewis acids. During the past few years, various catalysts [26–28] were used for the synthesis of 3-substituted indoles from α , β unsaturated carbonyl compounds including Lewis and Bronsted acid catalysts such as CuBr₂ [29], InBr₃ [3], [Al(DS)₃]·3H₂O [30], Au(III) [31], CeCl₃·7H₂O-NaI [2], SmI₃ [32,33] and K10-FeO [34]. Most of these reactions have been studied using highly nucleophilic indoles and yields are unsatisfactory. Recently Kantam et al.

ABSTRACT

Mesoporous Al-MCM-41 catalyzes the chemoselective Michael addition reaction between indoles and α,β -unsaturated ketones to afford β -indolylketones at room temperature with excellent yields. The higher catalytic activity is attributed to Lewis acidic Al and the large surface area. The catalyst is readily recovered and reused more than six times without loss in its catalytic activity. The substitution at the indole nucleus occurs exclusively at the 3-position and N-alkylation products are not observed.

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reported nano TiO₂ as a catalyst for Michael addition between indole and enone [35]. Use of lanthanide triflates [18,20,36] represents an attractive alternate to catalysts such as AlCl₃, TiCl₄ and SnCl₄. Unfortunately lanthanide triflates are expensive and their use in large scale methodology is limited. Consequently Lewis acid catalysts which are more cost efficient than lanthanide triflates are desirable. Many of the homogeneous systems for conjugate addition of indoles require careful control of acidity to prevent side reactions including dimerization or polymerization. Furthermore, many of the reported procedures with homogeneous catalysts involve drawbacks such as strong acidic conditions, expensive reagents, lower yield of products and longer reaction time [37]. Therefore, the development of an efficient, cost-effective and environmentally benign solid Lewis acid catalyst for Michael addition is desirable for this process.

Ordered mesoporous materials like MCM-41 are attractive heterogeneous solid catalysts for fine chemicals synthesis because their high surface area which ensure high dispersion of active sites while the large pores may facilitate the diffusion of reactant molecules from bulk solution onto the catalyst surface [38]. MCM-41 has a regular pore diameter of *ca*. 5 nm and a specific surface area >700 m² g⁻¹ [39,40]. Its larger pore size allows the passage of larger organic molecules and metal complexes through the pores to reach the surface of the channels [41–43]. For instance, aluminium substituted mesoporous silica acts as a solid acid catalyst for fine chemicals syntheses through Aldol [44], Friedel-Crafts [45], Diels-Alder [46] and acetalization reaction [47,48]. In continuation our interest in developing heterogeneous clays/zeolites based solid acid catalysts for organic transformations [49-53], herein we

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Table 1

Screening of reaction parameters with various catalyst for the formation of 3-(3-indolyl)-1,3-diphenylpropan-2-one.^a



Entry	Catalyst	Solvent	Time (h)	Yield (%) ^b
1	None	_	24	-
2	MCM-41 ^c	CH₃CN	12	18
3	SiO ₂	CH₃CN	12	10
4	Al_2O_3	CH ₃ CN	12	18
5	SiO ₂ -Al ₂ O ₃	CH ₃ CN	12	56
6	Na-Y ^c	CH₃CN	12	35
7	H–Y ^c	CH₃CN	12	40
8	Al-Y ^c	CH₃CN	10	71
9	Al-MCM-41 (100)	CH₃CN	1	30
10	Al-MCM-41 (75)	CH ₃ CN	1	55
11	Al-MCM-41 (50)	CH ₃ CN	1	68
12	Al-MCM-41 (25)	THF	2	76
13	Al-MCM-41 (25)	CH_2Cl_2	2	78
14	Al-MCM-41 (25)	Toluene	2	81
15	Al-MCM-41 (25)	n-Hexane	2	83
16	Al-MCM-41 (25)	DMF	2	80
17	Al-MCM-41 (25) ^d	CH₃CN	1	>5
18	Al-MCM-41 (25) ^e	CH₃CN	1	10
19	Al-MCM-41 (25) ^f	CH₃CN	1	44
20	Al-MCM-41 (25) ^g	CH₃CN	1	69
21	Al-MCM-41 (25) ^h	CH₃CN	1	95
22	Al-MCM-41 (25) ^h	CH₃CN	0.5	56
23	Al-MCM-41 (25) ⁱ	CH₃CN	10	10
24	Al-MCM-41 (25) ^j	CH ₃ CN	10	34

^a *Reaction conditions*: indole (1 mmol), chalcone (1 mmol), catalyst (100 mg), solvent 2 mL, room temperature.

^b Isolated yield.

 $^{c}\,$ Calcination at 450 $^{\circ}\text{C}$ for 6 h.

 $^d~20\,mg$ (calcination at 500 $^\circ C$ for 5 h) of the catalyst is used.

^e 40 mg (calcination at 500 °C for 5 h) of the catalyst is used.

 $^{\rm f}$ 60 mg (calcination at 500 $^\circ$ C for 5 h) of the catalyst is used.

^g 80 mg (calcination at 500 °C for 5 h) of the catalyst is used.

^h 100 mg (calcination at 500 °C for 5 h) of the catalyst is used.

ⁱ Al-MCM-41 catalyst used without calcination.

^j Calcination at 300 °C for 3 h.

describe the synthesis and characterization of mesoporous aluminium MCM-41, which is subsequently used for the Michael addition of indoles with, α , β -unsaturated carbonyl compounds at room temperature. This regioselective methodology is significant from an environmental point of view. It is also interesting to note that the catalyst is recovered and reused for several times without loss of activity.

2. Experimental

2.1. Materials

Sodium metasilicate (Na₂SiO₃·5H₂O, \geq 98% Sigma), aluminium sulphate (Al₂(SO₄)₃·18H₂O, \geq 98% Sigma), cetyltrimethylammonium bromide (C₁₆H₃₃(CH₃)₃N⁺Br⁻ \geq 99% Sigma), sulphuric acid (H₂SO₄, >98% Merck) all the chemicals are purchased as A.R. grade and other chemicals for Michael addition are purchased from Sigma–Aldrich (\geq 98%) and used without purification.

2.2. Characterization of materials

The XRD pattern of the catalyst samples is measured with a PW3050/60 (XPERT-PRO Diffractometer system) instrument using a Cu K α radiation at room temperature. The electron diffraction pattern is recorded for the selected area. NMR spectra are recorded on

Bruker DRX spectrometer operating at 300 MHz for ¹H and 75 MHz for ¹³C NMR. All ¹H NMR and ¹³C NMR spectra are measured in CDCl₃ with TMS as the internal standard. The aluminium content in Al-MCM-41 for Si/Al ratio 25 is recorded by ICP-AES with Allied Analytical ICAP-9000.

2.3. Synthesis of Al-MCM-41

The Al-MCM-41 (Si/Al ratio=25) is synthesis according to the previous report [53-55] with the gel composition of SiO₂:XAl₂O₃:0.2 CTAB:0.89 H₂SO₄:120H₂O using sodium meta silicate as the silicon source, H₂SO₄, cetyltrimethylammonium bromide as the structure directing agent and aluminium sulphate as the aluminium source. 21.21 g of sodium meta silicate is dissolved in 80 mL of water and allowed to stir for half an hour. Then required quantity of aluminium sulphate, which is dissolved in 15 mL of water, is added and allowed to stir for 1 h. Then 40 mL of 4N sulphuric acid is added drop by drop until the gel formed. The stirring is continued for 2 h. Exactly 7.28 g of cetyltrimethylammonium bromide (CTAB), dissolved in 25 mL of water is added and stirred for further 2 h. After that, the gel is transferred to an autoclave and it is kept in a hot air oven at 145 °C for 36 h. The obtained product is filtered, washed several times with double distilled water and dried at 80 °C in an air oven for 2 h. Then it

Table 2

Al-MCM-41 catalyzed Michael addition reaction of various substituted indoles with α , β -unsaturated ketones.^a



Table 2 (Continued)



^a Reaction conditions: indole (1 mmol), chalcone (1 mmol), Al-MCM-41 (100 mg), ACN (2 mL), room temperature.

^b Isolated yield.

is calcined in a muffle furnace at 550 °C for 6 h to remove the template. After synthesized Al-MCM-41 is characterized by powder XRD, nitrogen adsorption-desorption isotherm (BET), FT-IR, ICP-AES and SEM techniques (Figs. S.1–S.3, supporting information).

2.4. General procedure for the Al-MCM-41 catalyzed Michael addition of indoles with α , β -unsaturated ketones

Indole 1 mmol and chalcone 1 mmol are successively added to Al-MCM-41 100 mg (calcination at 500 °C in air for 5 h), 2 mL of acetonitrile and stirred at room temperature for 30–60 min, after completion of the reaction, the mixture is extracted with ethyl acetate. After removing the catalyst by simple filtration, followed by solvent evaporation the resulting crude product is obtained and purified by column chromatography (silica gel). The recovered catalyst is thoroughly washed with ethylacetate and used for the next run. The purified products are characterized by their ¹H and ¹³C NMR as well as by mass spectral data (S.6. and Figs. S.4–S.31 in supporting information).

3. Results and discussion

The efficiency of the Al-MCM-41 as catalyst in the Michael addition of indoles to unsaturated ketones has been explored. Indole (1) and chalcone (2) are selected as model substrates and are screened for a range of parameters such as effect of different catalysts, solvents and reaction times. The observed results are summarized in Table 1.

There is no reaction in the absence of any catalyst (Table 1, entry 1). Only a moderate conversion is observed with aluminium-free mesoporous silica (Table 1, entry 2). Silica (SiO₂) and alumina

 (Al_2O_3) sources are tested independently to promote the reaction and lesser amount of the product (10% and 18% respectively) are observed (Table 1, entries 3 and 4). On the other hand, SiO₂–Al₂O₃ affords an improved yield of 56% (Table 1, entry 5). These results clearly indicate that both the ordered mesoporous structure and the presence of aluminium are essential for promoting the Michael addition. Microporous zeolite catalysts such as Na–Y and H–Y are less effective (Table 1, entries 6 and 7). However the reaction is facile with Al–Y (Table 1, entry 8), whereas mesoporous Al-MCM-41 afford the desired Michael adduct in 95% yield. The catalytic activity observed with Al-MCM-41 having different Si/Al ratio, such as Al-MCM-41 (25) > Al-MCM-41 (50) > Al-MCM-41 (75) > Al-MCM-41 (100) is also reported (Fig. 1).

Lower yield in the presence of Al-MCM-41 with high Si/Al ratios (Table 1, entries 9–11 and 21) may be due to its high hydrophobicity, with which it can retain most of the reactants inside the pores thereby blocking their diffusion. We also screened different solvents to optimize the reaction conditions. Organic solvents such as THF, CH_2Cl_2 , toluene, DMF and acetonitrile resulted in formation of Michael adduct in moderate to good yields (Table 1, entries 12–16). Among them, acetonitrile affords the Michael adduct in an excellent yield of 95% within 1 h (Table 1, entry 21). Better catalytic performance is observed with 100 mg of Al-MCM-41 catalyst (Fig. 1) and the yield is also dependent on amount of catalyst (Table 1, entries 17–21).

This facile and clean protocol for the synthesis of 3-substituted indoles is extended to various substituted indoles and electron deficient α , β -unsaturated carbonyl compounds using Al-MCM-41 in acetonitrile at room temperature. The observed results are presented in Table 2. α , β -Unsaturated ketones with electron deficient (chloro, bromo and nitro) and electron rich (hydroxyl, methyl and methoxy) substituents react readily giving good to excellent yields



Fig. 1. Michael addition of indole to chalcone with various amounts of catalyst and Si/Al ratio of Al-MCM-41.

with high selectivity (Table 2, entries 1–8). It is observed that the substitution on the indole nucleus occurs exclusively at the 3position. 2-Methylindole gave higher amount of yields (Table 2, entries 2, 3, 8 and 10).

In case of a sterically hindered enone namely 3,4dichlorochalcone, the reaction proceeds smoothly with good yield within 1 hr (Table 2, entries 9 and 10). Among the various Michael acceptors, the reactions proceed smoothly with methyl vinyl ketone, cyclohexenone and cyclopentenone to afford corresponding Michael adducts within 30 min with excellent yields 91-94% (Table 2, entries 11-13). In all these cases of cyclic enones, the reactions proceed at room temperature with high selectivity. It is also important to note that products arising from 1,2-addition are not observed under conditions. The reactions are clean and the products are obtained in high yields, without formation of any side products such as N-alkylation product. This result provides an interesting contrast to similar reactions with palladium catalyst [56].

Table 3

Tuble 5	
Reusability of Al-MCM-41 catalyzed Michael addition reaction indole to chalcone	e.ª

Reuse	1st	2nd	3rd	4th	5th	6th	7th
Yield (%) ^b	95	94	94	92	90	89	87

^a Reaction conditions: indole (1 mmol), chalcone (1 mmol), Al-MCM-41 (100 mg, calcination at 300 °C for 5 h), ACN 2 mL, room temperature.

^b Isolated yield.

Table 4

Sheldon test.^a

Catalyst Al-MCM-41	Time		Reused catalyst (1 h)
	30 min	30 min + 2 h	
Yield (%) ^b	59	60	94

^a Reaction conditions: indole (1 mmol), chalcone (1 mmol), Al-MCM-41 (100 mg, calcination at 500 °C for 5 h), ACN 2 mL, room temperature.

Isolated yield.

Table 5

Co	mpariso	n witl	n reported	catalytic	systems	for l	Mic	hae	ad	ditio	n of	indo	ole v	with	α,	3-unsaturated	ketones.
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Entry	Catalyst	Solvent	Temp (°C)	Time (h)	Yield (%)	Reusability
1	CeCl ₃ ·7H ₂ O-NaI (30 mol%) [2]	CH ₃ CN	RT	2-48	>80	5
2	InBr ₃ (10 mol%) [3]	CH_2Cl_2	RT	16-24	65-90	NR ^a
3	ZrCl ₄ (0.02 mmol) [4]	CH_2Cl_2	RT	<1	<90	NR
4	Zn-HAP (1 mmol) [9]	CH ₃ CN	Reflux	4-36	98-18	2 (75) ^b
5	Ionic liquid (0.02 mmol) [11]	CH₃CN	80	4	90-98	3 (90) ^b
6	TMSCl (20 mol%) [16]	CH_2Cl_2	RT	24	97-55	NR
7	Nano TiO ₂ (10 mol%) [35]	CH_2Cl_2	RT	6	75-93	5 (71) ^b
8	[Bmim]HSO ₄ (10 mol%) [14]	EtOH	Reflux	3-6	>90	3 (51) ^b
9	H ₃ PW ₁₂ O ₄₀ (0.4 mol%) [26]	H ₂ O	RT	18	80-90	NR
10	SbCl ₃ (20 mol%) [27]	CH₃CN	Reflux	6-9	80-90	NR
11	Fe-Mg (10 mol%) [28]	CH₃OH	RT	12	99-64	NR
12	CuBr ₂ (0.45 mol) [29]	CH₃CN	RT	<1	52-68	NR
13	NaAuCl ₄ ·2H ₂ O (5 mol%) [31]	EtOH	RT	2-6	>80	NR
14	K10-FeO (0.5 g) [34]	CH₃CN	RT	1-5	73-90	NR
15	SmI ₃ (10 mol%) [33]	CH ₃ CN	MW	15 min	>80	NR
16	Bi(OTf) ₃ (5 mol%) [37]	CH₃CN	RT	1-5	>80	NR
17	NO ⁺ BF ₄ ⁻ (20 mol%) [55]	Ethyl ether	36	2-8	>90	NR
18	GaI ₃ (10 mol%) [54]	CH_2Cl_2	RT	1-3	80-90	NR
19	Al-MCM-41 (100 mg) ^c	CH₃CN	RT	>1	>90	7 (87) ^b

^a Not reported.

^b Percentage of yield after reused of the catalyst.

^c Our system.



Scheme 1. Plausible mechanism of role of Al-MCM-41 as a Bronsted acid (a) and Lewis acid (b) catalyst in Michael addition of indole to chalcone.

To account for the obtained results and by analogy with previous reports [5], two plausible reaction mechanisms are proposed involving Brønsted and Lewis acidic sites of Al-MCM-41 for Michael addition of indole to chalcone (Scheme 1). In the Bronsted acid catalyzed mechanism (Scheme 1a), the enone is activated by the acidic protons of Al-MCM-41. Indole then attacks the electron deficient conjugated carbon–carbon double bond *via* its β -position to afford (2), followed by H-transfer to give (3). Finally, (3) is rearranged to target compound (4) and the catalyst is recycled.

A Lewis acid catalyzed mechanism is also visualized (Scheme 1b). In this, Al-MCM-41 readily coordinates to O atom of α , β -unsaturated ketone, which reacts with indole through its β -position to form an intermediate (5), which upon subsequent electron reorganization followed by H-transfer yields (4), releasing the catalyst for the next cycle.

As recyclability is important for industrial applications of a good catalyst, reuse performance of Al-MCM-41 is investigated. After completion of reaction, catalyst is recovered by simple filtration, washed, dried and calcined at 500 °C and reused for next cycle. Even after the sixth recycle, it exhibits good catalytic activity with 87% yield as shown in Table 3.

In order to verify the true heterogeneity of the process, Sheldon test is performed on the reaction with the aim of evaluating possible metal leaching. The reaction mixture is filtered after 30 min and the filtrate is further stirred for an additional 2 h. The observed results indicate that no appreciable leaching of metal ions in the filtrate is noticed in the present reaction conditions (Table 4).

Data on reaction conditions, activity and efficiency of the different catalysts reported in literature for Michael addition of indole with α , β -unsaturated ketones are given in Table 5. Comparison of the results indicates that our catalytic system (entry 19) exhibits better activity compared to conventional catalysts which require higher reaction time (entries 1, 2, 4–11, 13, 14 and 17), higher temperature (entries 5, 8, and 10) and poor reusability of the catalyst (entries 2-5 and 8-18).

4. Conclusions

In this study, we have demonstrated a, very simple, mild reaction protocol with greater selectivity, short reaction time and efficiency for Michael addition of indoles to α,β -unsaturated ketones catalyzed by Al-MCM-41. The unique properties of present system are outlined as below: (a) the procedure is operationally simple and can furnish a wide variety of 3-substituted indole derivatives in good yields, (b) the catalyst can be recycled with comparable activity and (c) there is no need for any other additive to promote the reaction. This method is a practical alternative due its simplicity, environmental acceptability and inexpensiveness. This report clearly exhibits the promising abilities of mesoporous aluminosilicates as catalysts in organic synthesis, especially for fine chemical synthesis.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/ j.molcata.2012.05.024

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