

# Cage Like Al-KIT-5 Mesoporous Materials for C–C Bond Formation Reactions Under Solvent Free Conditions

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**Abstract** The C–C bond forming reactions are of fundamental importance in chemistry. As a result there is ever growing interest for chemists to develop new methods for C–C bond formation. We report here three dimensional nano-cage mesoporous aluminosilicate materials Al-KIT-5 which exhibited very good catalytic activity for Mukaiyama-aldol and Mukaiyama–Michael reactions under solvent free condition. Mukaiyama-aldol and Mukaiyama–Michael reactions of silyl ketene acetal with aldehyde and  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds produced  $\beta$ -hydroxy esters and 1, 5-dicarbonyl compounds, respectively in good yields. The product selectivity was found to be 100 % in a short reaction period. The high acidity, 3D pores, and a huge space in the nano-cages materials make them attractive candidate for carrying out important organic reactions. The catalyst provide a simple, easy to handle method, and could be used to solve the problems of corrosion, toxicity, waste production, and high cost that are being currently encountered by the conventional homogeneous catalysts.

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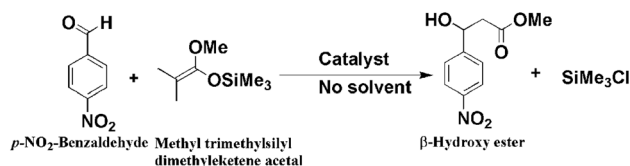
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## Graphical Abstract



**Keywords** Acid catalyst · Al-KIT-5 mesoporous materials · Mukaiyama-aldol and Michael reaction · Silyl ketene acetal · Silyl enol ether · Aldehyde and  $\alpha$  ·  $\beta$ -unsaturated carbonyl compounds

## 1 Introduction

Because of unique well-ordered 3D structure with high porosity, high specific surface area and pore volume of mesoporous materials, they have found wide range of applications in areas of adsorption, separation, sensing, fuel cells and catalysis [1–6]. 3D cage like KIT-5 mesoporous material with cubic Fm3m close packed symmetry has more advantages than hexagonal pore structures (MCM-41 and SBA-15) [1–7]. These materials allow faster diffusion of reactants, avoid pore blockage, provide more adsorption sites, and can be used for processing large-sized molecules [1–7]. Recently, Vinu et al. reported the KIT-5 mesoporous material by controlling the amount of HCl during synthesis of the material [4, 7, 8]. They also studied the amount of Al content, pore diameter and the morphology of the KIT-5 materials and observed superior catalytic activity than zeolites and Al-MCM-41 catalysts for acetylation reaction [4, 7]. Several other organic reactions including three component one-pot reaction of synthesis of  $\alpha$ -aminophosphonates,

ring opening of epoxides with indoles and primary amines over nano-cage mesoporous Al-KIT-5 catalysts [9–11] were also studied by this research group. Very recently, we observed excellent results for aza-Michael reaction catalysed over the same Al-KIT-5 mesoporous materials under solvent free condition [12]. Moreover, Kalita et al. reported the functionalization of mesoporous KIT-5 materials using super acid like triflic acid and found very good catalytic activities for the synthesis of coumarin via Pechmann reaction of resorcinol and ethyl acetoacetate under solvent free system [13].

Mukaiyama-aldol and Mukaiyama–Michael reactions are powerful methods for preparation of C–C bond in organic synthesis [14–16]. Mukaiyama-aldol reaction produces  $\beta$ -hydroxy/ $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds which are used for the preparation of several drug molecules [17]. The Michael product of 1, 5-dicarbonyl compounds can also serve as starting materials for total synthesis of the antitumor diterpenoid bruceantin and the cytotoxic natural product sesbanimide A [18, 19], preparation of bridged- or fused-ring bicyclic ketone [20], preparation of heterocyclic [21, 22] and polyfunctional compounds [23, 24].

Several authors have reported the reaction between silylenol ether or silyl ketene acetal with aldehydes and  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds using several homogeneous Lewis acid such as  $\text{TiCl}_4$ ,  $\text{SnCl}_4$ ,  $\text{Ti}(\text{O}-i\text{Pr})_4$ ,  $\text{Ti}(\text{OEt})_4$ , using stoichiometric amounts and at lower temperatures [14, 17]. Among the heterogeneous catalyst, solid acid catalysts such as amorphous  $\text{SiO}_2\text{--Al}_2\text{O}_3$  and zeolites are also known for promoting C–C bond formation [25–29]. However, only a few heterogeneous catalysts and inorganic salts, like  $\text{CsF}$ , Al-clay montmorillonite, metal-incorporated mesoporous materials & montmorillonite K10 have shown Mukaiyama-aldol reaction under different reaction conditions [30–33].

Recently, Kalita et al. showed exciting catalytic activities for Mukaiyama-aldol and Michael reaction using calcined Ce–Al-MCM-41 catalyst under solvent free and solvent system, respectively [34, 35]. Sn-incorporated into different kinds of 2D (MCM-41) and 3D (MCM-48) mesoporous materials have potential capacity for Mukaiyama-aldol reaction under solvent free condition [36, 37]. Corma and co-workers have reported the same reaction using heterogeneous solid oxophilic Lewis acid catalyst such as Ti-MCM-41 [38]. Zeolytic microporous materials like titanium silicate molecular sieve (TS-1) is also responsible for catalyzing the C–C bond formation in Mukaiyama type aldol and Michael reactions and reported by Kumar et al. [39–41]. Over this TS-1 catalyst, they were able to report distereoselective syn/anti product in the case of aldol reaction.

Many of the above methods suffered from drawbacks, such as they need large excess of reagents, extreme precaution for making the catalyst, long reaction time,

environmental pollution, etc. Here, we report a synthetic methodology for preparation of  $\beta$ -hydroxy esters and 1, 5-dicarbonyl compounds through Mukaiyama-aldol and Michael reaction by utilization of the highly acidic Al-incorporated KIT-5 catalysts addressing many of these issues. The catalyst was found to be highly active with 100 % of product selectivity and affording excellent yield in short reaction time.

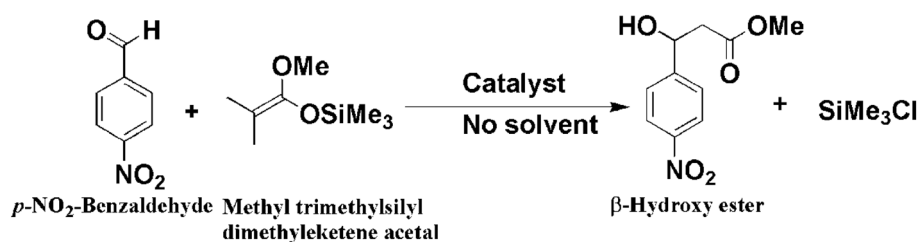
## 2 Experimental

### 2.1 Synthesis of Al-KIT-5 Catalyst and Characterization

Al-incorporated highly ordered mesoporousKIT-5 catalyst was synthesised using pluronic F127 ( $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$ , molecular weight 12,500), and tetraethyl orthosilicate and aluminium isopropoxide as a structure directing agent, and the sources of silica and aluminium, respectively. The materials were obtained from Sigma-Aldrich chemicals, Bangalore, India and used without further purification. The detailed synthesis procedure and characterization of the textural properties of the materials is available in the recent literature [4, 8, 12]. Al-KIT-5(10) where the number in the parenthesis denotes the Si/Al ratio was used in our previous study [4, 8–12]. In a typical synthesis, 5.0 g of F127 is dissolved in the required amount of HCl (35 wt%) and 240 g of distilled water. To this mixture, 24.0 g of TEOS and the required amount of the desired Al source were added, and the resulting mixture was stirred for 24 h at 373 K. Subsequently, the reaction mixture was heated for 24 h at 373 K under static condition for hydrothermal treatment. The solid product was filtered off and then dried at 373 K without washing. The product was calcined at 813 K for 10 h. Moreover, we also synthesised Si/Al ratio 28 and 44 for comparison studies.

### 2.2 General Procedure for Mukaiyama-aldol Reaction

The catalytic reaction was performed in liquid-phase using a two-necked continuously stirred round bottom flask, equipped with a water condenser. The catalyst was pre-activated at 393 K in a vacuum oven and the reactions were carried out under  $\text{N}_2$  atmosphere. In a typical procedure, the methyl trimethylsilyl dimethylketene acetal (10 mmol) was added to a pre-activated catalyst (0.1 g), followed by addition of *p*- $\text{NO}_2$ -benzaldehyde (10 mmol) to reaction vessel. The reaction mixture was stirred at 373 K for a period of 6 h. The progress of the reaction was monitored by thin layer chromatography (TLC). After completion of the reaction, the catalyst was filtered out and the filtrate

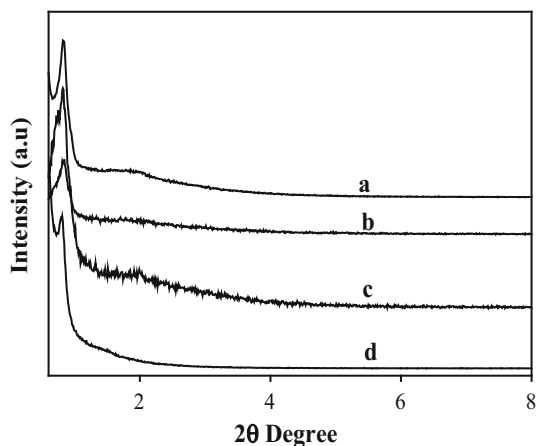


**Scheme 1** Solvent-free Mukaiyama-aldol reaction of methyl trimethylsilyl dimethylketene acetal with *p*-NO<sub>2</sub>-benzaldehyde

was diluted with DCM and then washed with 1 N HCl and finally washed with water. The organic layer was separated and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by rotary evaporator and the product was purified through column chromatography using silica gel (100–200 mesh) as a stationary phase and petroleum ether + ethyl acetate (4:1) as eluent. The final products were identified with the help of <sup>1</sup>H and <sup>13</sup>C NMR and compared with literature data (Scheme 1) (see Supporting information).

### 3 Results and Discussion

Powder X-ray diffraction patterns were collected on a Rigaku diffractometer using Cu Kα ( $\lambda = 0.15406$  nm) radiation, operated at 40 kV and 40 mA. The diffractograms were recorded in the 2θ range of 0.7°–10° with a 2θ step size of 0.01° and a step time of 6 s. The calcined samples show well-ordered characteristic properties of mesoporous materials with well-ordered cage type three dimensional silica networks and it is shown in Fig. 1. From XRD pattern it is seen that the peaks are slightly shifted towards lower 2θ values with increasing Al-content in the Al-KIT-5 samples which increases the unit cell constant parameters. This is due to the formation of Al–O bond in the silica network which is longer than Si–O bonds.



**Fig. 1** The powder XRD patterns of the calcined Al-KIT-5 samples of *a* pure KIT-5, *b* Al-KIT-5 (44), *c* Al-KIT-5 (28) and *d* Al-KIT-5 (10)

The nitrogen adsorption–desorption isotherms were measured at –196 °C on a Quantachrome Autosorb 1 volumetric adsorption analyzer. The surface area of synthesized catalyst was determined by BET technique and surface areas of calcined Al-KIT-5 (10), Al-KIT-5 (28) and Al-KIT-5 (44) catalysts were 989, 815 and 713 m<sup>2</sup>g<sup>–1</sup>, respectively [4, 8]. The details of characterization of Al-KIT-5 catalysts and their physicochemical data were reported by Vinu et al. [4, 8] and are not shown here. The total acidity of the calcined Al-KIT-5 samples were determined through temperature-programmed desorption (NH<sub>3</sub>-TPD) techniques using Micromeritics Autochem 2910 instrument. The total acidities of calcined Al-KIT-5 (10), Al-KIT-5 (28) and Al-KIT-5 (44) catalysts were 0.50, 0.32 and 0.14 mmolg<sup>–1</sup>, respectively [4].

#### 3.1 Catalytic Activity

##### 3.1.1 Screening of the Catalysts

The catalytic activity of different Al-content calcined Al-KIT-5 catalyst was examined for Mukaiyama-aldol reaction of methyl trimethylsilyl dimethylketene acetal with *p*-NO<sub>2</sub>-benzaldehyde and the results are given in Table 1. The reaction was carried out at 373 K under solvent free condition for 6 h. The progress of the reaction was monitored by thin layer chromatography (TLC). The percentage of yield of the desired product is found to have increased with increasing the mole ratio of Al/Al + Si in KIT-5 catalyst. This is clearly observed by plotting of percentage of yield against the mole ratio of Al/Al + Si in Fig. 2. The yields of products were 71, 80 and 88 % for Al-KIT-5 (44), Al-KIT-5 (28), Al-KIT-5 (10) catalysts respectively (Table 1, Entries 2–4). However, the turn over number (TON) for individual catalyst is calculated to know the better understanding of catalytic activity of each reaction and shown in Table 1. High yields under solvent free condition could be explained due to the more interaction between substrate with active catalyst. We observed similar result when we conducted the same reaction in the identical reaction condition over calcined Ce–Al-MCM41 catalyst [34]. However, in this case we reported 98 % of product selectivity which was based on GC analysis. Although the

**Table 1** Screening of different catalysts for Mukaiyama-aldol reaction of methyl trimethylsilyl dimethylketene acetal with *p*-NO<sub>2</sub>-benzaldehyde

Entries	Catalyst	Solvent	Al/Al + Si (mole/mole). 10 <sup>-3</sup>	Yields (%) <sup>a</sup>	TON <sup>c</sup>
1.	No catalyst	No solvent	–	8 <sup>b</sup>	–
2.	Al-KIT-5 (44)	No solvent	0.37	71 <sup>b</sup>	191
3.	Al-KIT-5 (28)	No solvent	0.57	80 <sup>b</sup>	139
4.	Al-KIT-5 (10)	No solvent	1.51	88 <sup>b</sup>	58
5.	ZSM-5	No solvent	nd <sup>d</sup>	45 <sup>b</sup>	nd <sup>d</sup>
6.	Mordenite	No solvent	nd <sup>d</sup>	50 <sup>b</sup>	nd <sup>d</sup>

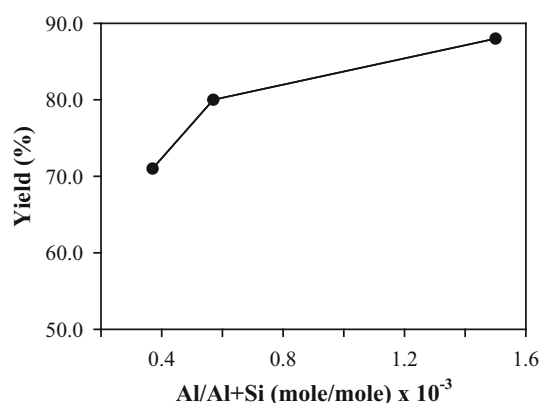
Reaction conditions: methyl trimethylsilyl dimethylketene acetal (10 mmol), *p*-NO<sub>2</sub>-benzaldehyde (10 mmol), 100 mg of catalyst, no solvent, 373 K

<sup>a</sup> Isolated yield

<sup>b</sup> 6 h

<sup>c</sup> TON (turn over number) is calculated in terms of moles of reactant converted with respect to per mole of active Al-site

<sup>d</sup> Not determined

**Fig. 2** Plot of yield (%) versus Al/Al + Si (mole/mole) × 10<sup>-3</sup>

total acidity of Ce incorporated Al-MCM41 catalyst is less (0.419 mmol g<sup>-1</sup>) than Al-KIT-5 (0.50 mmol g<sup>-1</sup>) catalyst which is similar to the results in this present work. This is due to the synergistic effect by simultaneous incorporation of Ce and Al in MCM-41 silica network which created more acidic sites in catalyst [34, 42]. The less yield observed in the present result is may be due to the loss of compound on handling process by separation of pure compound by column chromatography. However, we also carried out the blank experiment of the same Mukaiyama-aldol reaction without using any catalyst under solvent free system in the identical reaction condition for a period of 6 h. We observed significantly low yield of 8 % of desired product (Table 1, Entry 1). Of the Al-KIT-5 catalysts studied, Al-KIT-5 with Si/Al (10) found to be the best catalyst for this particular Mukaiyama-aldol reaction and we observed the same trend in our previous studies with the same Si/Al ratio 10 [4, 8–12]. The higher activity of Al-KIT-5 catalysts could be mainly attributed to their excellent structural order with 3D pore symmetry and highly

dispersed active sites on the uniform pore surface, which are easily accessible for the reactant molecules. The high yield of aldol product could also be explained due to the total acidity of Al-incorporated KIT-5 materials. The total acidity of Al-KIT-5 materials is increased by decreasing the Si/Al ratio and the results are adequately reported by Vinu et al. in his previous studies. The same research group concluded that Al is in tetrahedral position in Al-KIT-5 materials which are confirmed by temperature programmed desorption (TPD) and solid state NMR spectroscopy. These catalytic results also confirm that the Al-KIT-5 (10) material indeed possesses higher amount of tetrahedral Al, which provide the Bronsted acid sites [4, 8–12]. The same trends of results were observed for three component one-pot synthesis of  $\alpha$ -aminophosphonates [9], ring opening of epoxides with indoles and amines [10, 11] and acetylation of veratrole [4, 8] and aza-Michael reaction [12], etc. Moreover, the same Mukaiyama-aldol reaction of methyl trimethylsilyl dimethylketene acetal with *p*-NO<sub>2</sub>-benzaldehyde was examined with other catalysts for comparison purpose in the identical reaction condition (Table 1, Entries 5 & 6). It is observed that mordenite produced moderate yield of aldol product of 50 % than ZSM-5 of 45 %. This is may be due to the larger pore size of the mordenite materials. Hence, the catalyst Al-KIT-5 (10) was used for further studies of Mukaiyama-aldol reactions. From the above discussion, it is found that the high mole ratio of Al/Al + Si with catalyst AlKIT-5 (10) is carrying the less TON than other AlKIT-5 (28) and AlKIT-5 (44) catalysts. The decrease in TON may be due to the high agglomeration of metal particles in the surface of the mesoporous KIT-5 material although it has high total acidity and it was determined by TPD of ammonia [4]. The similar trend of TON was observed in our previous studies for synthesis of coumarin and Michael-addition reaction [43–45].

Scheme 2 represents the plausible reaction mechanism of the Mukaiyama-aldol reaction of methyl trimethylsilyl dimethylketene acetal with *p*-NO<sub>2</sub>-benzaldehyde for the formation of  $\beta$ -hydroxy ester compounds. In the initial step, the oxygen atom of carbonyl carbon (C = O) is activated in the presence of acid sites in the reaction media making the carbonyl carbon more electropositive (electron deficient). Furthermore, the lone pair electron of oxygen atom of silyl ether group is delocalized (due to the presence of electropositive silicon atom) thus making the C-2 carbon more electron rich. In the second step, the nucleophilic attack takes place from C-2 position of silyl ketene acetal to highly electropositive carbonyl carbon of *p*-NO<sub>2</sub>-benzaldehyde to produce the intermediate compounds of silyloxy form of Mukaiyama-aldol product. Finally, hydrolysis of the silyloxy intermediate with 1 N HCl yields the required Mukaiyama-aldol product of  $\beta$ -hydroxy ester and chlorotrimethylsilane (SiMe<sub>3</sub>Cl) as by-product.

### 3.2 Effect of Catalyst Amount

The Mukaiyama-aldol reaction of methyl trimethylsilyl dimethylketene acetal with *p*-NO<sub>2</sub>-benzaldehyde was investigated over different amount of Al-KIT-5 (10) catalyst and the results are given in Table 2. Individual reaction was carried out under solvent free condition in the identical reaction condition. The reaction was initially investigated with lower amount such as 25 mg of catalyst and product yield was found to be 56 %. To understand the effect of

**Table 2** Effect of catalyst amount for Mukaiyama-aldol reaction of methyl trimethylsilyl dimethylketene acetal with *p*-NO<sub>2</sub>-benzaldehyde over Al-KIT-5 (10) catalyst

Entries	Catalyst amount (mg)	Yields (%) <sup>a</sup>	TON <sup>c</sup>
1.	25	56 <sup>b</sup>	147
2.	50	71 <sup>b</sup>	93
3.	75	83 <sup>b</sup>	73
4.	100	88 <sup>b</sup>	58

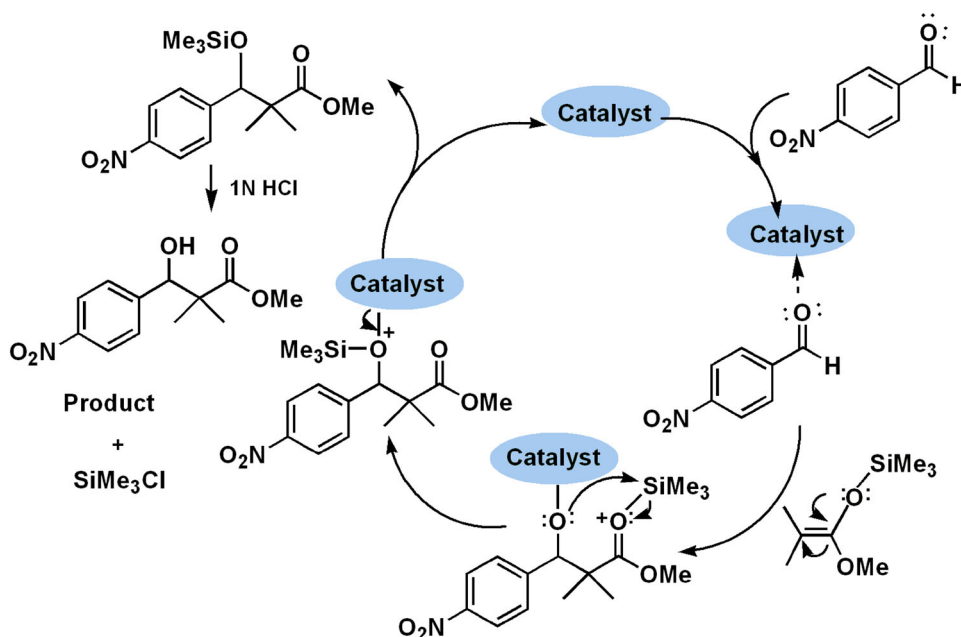
Reaction conditions: methyl trimethylsilyl dimethylketene acetal (10 mmol), *p*-NO<sub>2</sub>-benzaldehyde (10 mmol), no solvent, 373 K

<sup>a</sup> Isolated yield

<sup>b</sup> 6 h

<sup>c</sup> TON (turn over number) is calculated in terms of moles of reactant converted with respect to per mole of active Al-site

catalyst amount for this particular reaction, we have calculated the TON and given in the Table 2. While increasing the amount of catalyst from 25 mg to 100 mg, the satisfactory yield of desired product obtained as mentioned in Table 2. The high yield could be explained on the basis more interaction of the reactant molecules with the active sites of the Al-KIT-5 (10) catalyst in the reaction mixture. As we increased the catalyst amount from 75 mg to 100 mg, the availability of the active site of the catalyst getting saturated in the reaction mixture as indicated by the increase in yield from 56 to 88 %, respectively. The similar kinds of results were observed in our previous studies [4, 8–13, 34, 43–45].



**Scheme 2** Plausible mechanism for Mukaiyama-aldol reaction of methyl trimethylsilyl dimethylketene acetal (silyl ketene acetal) and *p*-NO<sub>2</sub>-benzaldehyde (aldehyde)



### 3.3 Effect of Reaction Temperature

The role of temperatures for Mukaiyama-aldol reaction of methyl trimethylsilyl dimethylketene acetal with *p*-NO<sub>2</sub>-benzaldehyde was examined over 100 mg of calcined Al-KIT-5 (10) catalyst under solvent free condition. The yields of the products obtained at each reaction temperature with TON are given in Table 3. The reaction was stirred for a period of 6 h and progress of the reaction monitored by thin layer chromatography (TLC). As expected, the product of Mukaiyama-aldol reaction increased from 51 to 88 % with increasing the temperature from 313 to 373 K (Table 3). This indicates that the catalyst is quite stable and the reaction was free from the diffusion limitation at higher temperatures. Furthermore, these results clearly showed that the active sites are getting activated with increasing temperatures from 313 to 373 K, which leads to a higher rate of attack of nucleophile (silyl ketene acetal) to carbonylation of carbonyl aldehyde (*p*-NO<sub>2</sub>-benzaldehyde). Therefore, the results in this table clearly show that Al-KIT-5 (10) catalyst could be used even at 373 K without compromising the yield of the desired product.

### 3.4 Recycle Studies

To find out the structure stability and regeneration of active sites of the calcined Al-KIT-5(10) catalyst, the recycling experiments were conducted for three consecutive cycles under the identical reaction condition. The yield of the each recycle and TON are given in Table 4. However, TON remained almost unchanged for each recycle. After the reaction, the catalyst was easily separated by centrifugation and reused without any further activation. It can be seen from the Table 4 that the yield of Mukaiyama-aldol product decreased as the number of cycles increased. This result is the indication of stability of the Al-KIT-5(10)

**Table 3** Effect of temperatures for Mukaiyama-aldol reaction of methyl trimethylsilyl dimethylketene acetal with *p*-NO<sub>2</sub>-benzaldehyde over Al-KIT-5 (10) catalyst

Entries	Temperature (K)	Yields (%) <sup>a</sup>	TON <sup>c</sup>
1.	313	51 <sup>b</sup>	33
2.	333	74 <sup>b</sup>	48
3.	353	84 <sup>b</sup>	55
4.	373	88 <sup>b</sup>	58

Reaction conditions: methyl trimethylsilyl dimethylketene acetal (10 mmol), *p*-NO<sub>2</sub>-benzaldehyde (10 mmol), 100 mg of catalyst, no solvent, 373 K

<sup>a</sup> Isolated yield

<sup>b</sup> 6 h

<sup>c</sup> TON (turn over number) is calculated in terms of moles of reactant converted with respect to per mole of active Al-site

**Table 4** Recycle studies for Mukaiyama-aldol reaction of methyl trimethylsilyl dimethylketene acetal with *p*-NO<sub>2</sub>-benzaldehyde over Al-KIT-5 (10) catalyst

Recycles no.	Yields (%) <sup>a</sup>	TON <sup>c</sup>
Fresh	88 <sup>b</sup>	58.0
1st	84 <sup>b</sup>	57.9
2nd	81 <sup>b</sup>	57.8
3rd	80 <sup>b</sup>	57.6

Reaction conditions: methyl trimethylsilyl dimethylketene acetal (10 mmol), *p*-NO<sub>2</sub>-benzaldehyde (10 mmol), no solvent, 373 K

<sup>a</sup> Isolated yield

<sup>b</sup> 6 h

<sup>c</sup> TON (turn over number) is calculated in terms of moles of reactant converted with respect to per mole of active Al-site

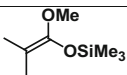
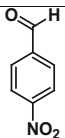
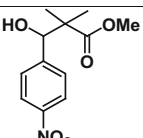
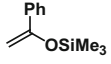
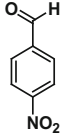
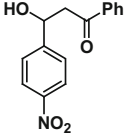
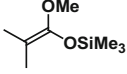
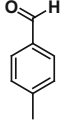
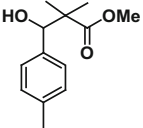
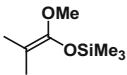
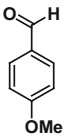
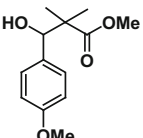
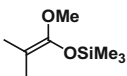
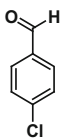
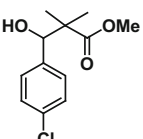
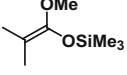
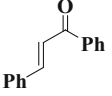
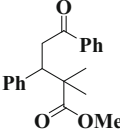
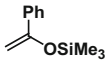
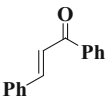
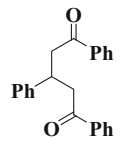
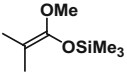

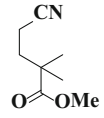
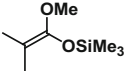

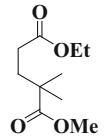
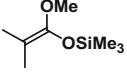

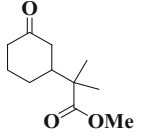
catalyst even after three consecutive cycles at 373 K. The decrease in yield of product could be due to the partial leaching of Al from the framework and blockage of pores in the channels of the catalyst by adsorption of reactants/products. In our recent publications, similar trends were observed for recycle studies over the same Al-KIT-5 catalyst for the different types of reactions like one pot three component reaction, Friedel-Craft alkylation of indole, ring opening of epoxide with amines and aza-Michael reaction [9–12] etc. In addition, we have also carried out to scale up the Mukaiyama-aldol product with 10 gm of methyl trimethylsilyl dimethylketene acetal and other reactant *p*-NO<sub>2</sub>-benzaldehyde and catalyst Al-KIT-5 catalysts were taken accordingly. We obtained ca. 85 % of product which is almost similar to the reported yield in Table 1 (Entry 4), revealing that the catalyst could easily be commercialized.

### 3.5 Effect of Different Substrates

Initially, the Mukaiyama-aldol reactions were investigated with *p*-NO<sub>2</sub>-benzaldehyde with different silyl compounds such as methyl trimethylsilyl dimethylketene acetal and 1-phenyl-1-trimethylsilyloxyethene under the solvent free system in the identical reaction condition (Table 5). Individual experiments were conducted for each reaction for a period of 6 h. The main reason for choosing *p*-NO<sub>2</sub>-benzaldehyde in this study is that it has more electropositive character on carbon atom of the carbonyl group (C = O) due to presence of very strong electron-withdrawing NO<sub>2</sub> group in the *p*- position on the benzene ring which facilitate faster nucleophilic addition of the silyl ketene acetal to the carbonyl group.

Higher yield was obtained when reaction was performed with methyl trimethylsilyl dimethylketene acetal (Table 5, Entry 1) and *p*-NO<sub>2</sub>-benzaldehyde than 1-phenyl-1-trimethylsilyloxyethene (Table 5, Entry 2). This result is in agreement with our previously published report [34]. It

**Table 5** Mukaiyama-aldol and Michael reactions over Al-KIT-5 (10) catalyst

Mukaiyama-aldol reactions				
Entry	Silyl ketene acetal / Silyl enol ether	Aldehydes / $\alpha$ , $\beta$ -Unsaturated carbonyl compound	Products	Yields (%) <sup>a</sup>
1.				88
2.				79
3.				82
4.				78
5.				84
For Mukaiyama-Michael reactions				
6.				92
7.				89
8.				87
9.				84
10.				61

Reaction conditions: silyl ketene acetal/silyl enol ether (10 mmol), aldehyde/ $\alpha$ ,  $\beta$ -unsaturated carbonyl compound (10 mmol), 100 mg of catalyst, no solvent, 373 K, 6 h

<sup>a</sup> Isolated yield

may be due to the presence of more negative character on the  $\beta$ -carbon in case of methyl trimethylsilyl dimethylketene acetal than 1-phenyl-1-trimethylsilyloxyethene. In the former case, the  $\beta$ -carbon is attached with the electron-donating (+I effect) methyl group, making the nucleophilic addition more preferable (Table 5, entry 1). On the other hand, low yield was observed when an electron-withdrawing phenyl group was attached to the  $\beta$ -carbon of silyl enol ether (Table 5, Entry 2). Hence, silyl compounds such as methyl trimethylsilyl dimethylketene acetal was considered for Mukaiyama-aldol reaction with different aldehydes.

To extend the Mukaiyama-aldol reaction, we have conducted the reaction between different aldehydes with methyl trimethylsilyl dimethylketene acetal over calcined Al-KIT-5 (10) catalyst under the same reaction condition. It is seen from Table 5 that *p*-Me-benzaldehyde (Entry 3) produced more aldol product than *p*-OMe-benzaldehyde (Entry 4) [34]. This could be explained on the basis of electron donating power OMe group attached to the benzene ring is more than the Me group. The presence of lone pairs in the OMe group makes the carbonyl carbon (C = O) less electrophilic due to delocalisation of lone pair electrons on oxygen atom to this centre. As a result, the nucleophilic addition silyl ketene acetal is more easier in *p*-Me-benzaldehyde. Moreover, we obtained high yield of aldol product when reaction was performed between *p*-Cl-substituted benzaldehyde (Table 5, entry 5) with methyl trimethylsilyl dimethylketene acetal than *p*-Me or *p*-OMe-benzaldehyde. This is mainly due to the high electronegativity group (–Cl) is attached to the benzene ring [34].

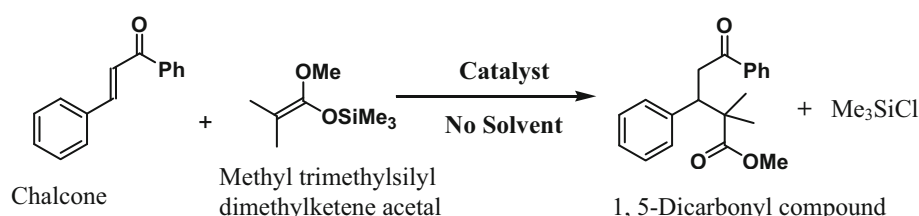
### 3.6 Mukaiyama–Michael Reaction

Mukaiyama-aldol and Mukaiyama–Michael reaction are known to be catalysed by acidic catalyst. Because of having high acidic properties of calcined Al-KIT-5 catalyst, we found promising results for Mukaiyama-aldol reaction. The results obtained prompted us to believe that this catalyst should also be a promising candidate for Mukaiyama–Michael reaction. Thus, we have carried out Mukaiyama–Michael reaction of methyl trimethylsilyl dimethylketene acetal with chalcone ( $\alpha$ ,  $\beta$ -unsaturated

carbonyl compounds) under solvent free condition using the identical reaction condition to produce 1, 5-dicarbonyl compounds (Scheme 3). The purpose of choosing chalcone is that attack of nucleophile (silyl ketene acetal) to electrophile (chalcone) via 1, 4-addition will be more faster (Table 5, Entry 6). Since, chalcone consist of two electron-withdrawing (phenyl) groups at both ends. As a result, electropositive character at C-1 carbon increases which facilitate more nucleophilic addition reaction to produce high yield of Mukaiyama–Michael product. Moreover, the same Mukaiyama–Michael reaction (Table 5, Entry 7) was performed between 1-phenyl-1-trimethylsilyloxyethene and chalcone ( $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds). As expected, the low yield of Michael product observed. Similar trend was observed in the case of Mukaiyama-aldol reaction Ce–Al-MCM41 catalysts in our previous study [35]. Due to synergistic effect by simultaneous incorporation of Ce and Al into the MCM-41 network, the calcined Ce–Al-MCM41 catalysts showed very promising results for the same Mukaiyama-aldol and Michael reaction and reported in our previous study [34, 35, 42]. As proposed mechanism for Mukaiyama-aldol reaction in the Scheme 2, we believe that Mukaiyama–Michael reaction also follows the similar type of mechanism.

To investigate the generality of the calcined Al-KIT-5 (10) catalyst, the Mukaiyama–Michael reaction of different  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds with methyl trimethylsilyl dimethylketene acetal was investigated under solvent free system in the identical reaction condition and the results are given in Table 5. It is evident that acrylonitrile (Table 5, Entry 8) produced more Michael product than ethyl acrylate (Table 5, Entry 9). It is due to the presence of strong electron withdrawing (–CN) group attached to the carbonyl (C = O) making the  $\beta$ -carbon more electron deficient. As a result, attack of nucleophile to electrophile is more facile. Moreover, we also investigated with cyclic  $\alpha$ ,  $\beta$ -unsaturated carbonyl compound such as cyclohexenone (Table 5, Entry 10) and obtained satisfactory yield of desired product.

From these results, we can strongly prove that three dimensional aluminosilicate mesoporous materials Al-KIT-5 (10) catalyst is also one of the useful heterogeneous catalysts for the formation of carbon–carbon bond through



**Scheme 3** Solvent-free Mukaiyama–Michael reaction of methyl trimethylsilyl dimethylketene acetal with chalcone



Mukaiyama-aldol and Michael reaction. As seen from Table 5, this Al-KIT-5 (10) catalyst can be utilized for a wide range of substrates giving desired aldol and Michael products. It also suggests that this reaction methodology avoids the necessity of solvents, highly expensive and toxic reagents. Moreover, the work is in progress to elaborate this process using different kinds of silyl ketene acetal or silyl enol ether and o- and m-substituted aldehydes or  $\alpha$ ,  $\beta$ -unsaturated carbonyl compound to produce aldol and Michael products, and detail work will be communicated soon.

The representative NMR data for both Mukaiyama-aldol and Michael reactions are compared with the literatures and given in supporting information.

## 4 Conclusion

Nano-cage three dimensional Al-incorporated mesoporous material synthesized which have potential character of large pores, high surface area, large pore volume, and a high acidity. These materials have been investigated for the preparation of  $\beta$ -hydroxy ester and 1, 5-dicarbonyl compounds through the Mukaiyama-aldol and Michael reaction, respectively. Among the various catalysts screened, the sample Al-KIT-5 (10) catalyst showed higher catalytic activity. This is due to the higher acidity of the catalyst. The product yield was raised by simply increasing the reaction temperature under the solvent free condition. Further, higher conversions were observed when electron-withdrawing ( $-I$  effect) groups are attached to the benzene ring of aldehyde and  $\beta$ -position of  $\alpha$ ,  $\beta$ -unsaturated carbonyl compound for aldol and Michael reactions, respectively.

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