

# Optimal synthesis parameters and application of Sn-MCM-41 as an efficient heterogeneous catalyst in solvent-free Mukaiyama-type aldol condensation

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## Abstract

Hydrothermal synthesis of mesoporous Sn-MCM-41 materials was established by optimizing crucial synthesis parameters. Several synthesis compositional variables such as molar TMAOH/SiO<sub>2</sub>, CTMABr/SiO<sub>2</sub>, H<sub>2</sub>O/SiO<sub>2</sub> and SiO<sub>2</sub>/SnO<sub>2</sub> ratios in the starting gel, type of silica and/or tin sources and synthesis time whose cause and effect relationship on the properties of Sn-MCM-41 materials have been explored. Gels with molar compositions SiO<sub>2</sub>:wSnO<sub>2</sub>:xCTMABr:yTMAOH:zH<sub>2</sub>O where 0.00 < w < 0.01, 0.18 < x < 0.32, 0.25 < y < 0.35, 25 < z < 45 were prepared and subjected for hydrothermal treatment at 383 K. Under identical and judiciously pre-optimized synthesis conditions, the influence of different combinations of silicon sources and tin sources on structural properties, tin configuration and morphology of Sn-MCM-41 has been investigated. Powder XRD, DRUV-vis, AAS, SEM and low temperature N<sub>2</sub> adsorption/desorption isotherms have been employed to characterize the products. Selected Sn-MCM-41 materials prepared using different silica and tin sources were evaluated for their efficiency in Mukaiyama-aldol condensation of methyl trimethylsilyldimethyl ketene acetal and benzaldehyde under solvent-free system. Invariably, the β-hydroxy ester selectivity was found to be 100% irrespective of the conversion levels. Among different source combinations, Sn-MCM-41 prepared with: (1) fumed silica and tin tetrachloride and (2) fumed silica and tin *tert*-butoxide have shown higher catalytic activity. The differences in the catalytic behavior of the materials were found to depend on tin content, the intrinsic differences in Sn siting and textural properties. Sn-MCM-41 materials have shown noticeable morphological differences upon changing the silica sources.

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**Keywords:** Hydrothermal synthesis; Characterization; Mukaiyama-aldol condensation; Synthesis parameters

## 1. Introduction

MCM-41 is a member of the M41S family of mesoporous molecular sieves [1,2], the discovery of which has brought about the beginning of a new age in the porous materials. The novelty of MCM-41 lies in the fact that, they possess a hexagonal arrangement of uni-dimensional mesopores with diameters ranging from 20 to 100 Å, large internal surface area, high thermal stability and favorable uniformity but easily tunable pore size. By virtue of these characteristics, it has attracted considerable interest in material science, heterogeneous catalysis and other relevant areas [3–7]. The challenges associated with synthesizing new molecular sieves and developing new syn-

thetic strategies for known molecular sieves possessing unique pore size distribution coupled with their thermal, structural and compositional peculiarities continue to attract the attention not only in scientific communities but also in industries. Exploring the cause and effect relationship between various synthesis parameters and properties of MCM-41 materials constitute the essence of current research in the field of mesoporous molecular sieves. Since Si-MCM-41 possesses a neutral framework, it has been used as a catalyst support rather than as a catalyst. In view of making them potential catalysts for various suitable applications, a great deal of research has been focused on the incorporation of various hetero-atoms into the silicate framework. In this connection, fewer investigations were devoted to the preparation, characterization and application of hetero-atoms such as Sn [8], Ti [9–11], V [12], B [13,14], Fe [15], Mn [16], etc. containing analogs of MCM-41. Sn-containing analogs of MCM-41 (Sn-MCM-41) were found to be a good catalyst

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for hydroxylation of phenol and 1-naphthol and the epoxidation of norbornene [8]. However, the applications of these mesoporous stannosilicate molecular sieves in areas other than the oxidation/epoxidation catalysis have not been explored yet. The Mukaiyama-type aldol reaction [17–19] of silyl enol ethers and aldehydes is a facile method for C–C bond formation. Under homogeneous conditions, some success has been achieved by using a variety of Lewis acids such as  $\text{TiCl}_4$ ,  $\text{SnCl}_4$  and  $\text{ZnCl}_4$  in stoichiometric ratio [20–23] at low temperature. A few heterogeneous catalysts such as clay, Nafion-117 and  $\text{SiO}_2\text{-Al}_2\text{O}_3$  have also been reported [24–27] at low temperature. Recently, the activities of titanium silicate molecular sieves have been reported in Mukaiyama-type aldol condensation [28–31]. Well-prepared Ti-MCM-41 catalysts were found to be more active than corresponding titanosilicate molecular sieves with MFI and BEA type structures for the Mukaiyama reaction [31]. On the other hand, among several Lewis acids, Sn within the zeolitic framework has shown the ability to polarize the carbonyl group making it more reactive towards hydrogen peroxide attack [32]. Moreover, from model cyclohexanol dehydration reaction,  $\text{Sn}^{4+}$  species were noticed to be more acidic than  $\text{Ti}^{4+}$  ions in MFI-type structures [33]. Interestingly, enhanced structural stability has been shown [34] by Sn-infused MCM-41. In spite of having higher structural stability and Lewis acid type properties which are potentially useful for catalytic purposes, a fewer number of studies deal with optimization of synthesis parameters for and catalytic application of Si-MCM-41 with partially substituted Sn. Prompted by this, we have investigated for the first time, an efficiency of Sn-MCM-41 for carbon–carbon bond formation in heterogeneously catalyzed Mukaiyama-aldol condensation reaction. Nonetheless, even if, the benefits of use of Sn-MCM-41 as efficient catalyst for this reaction are expected due to well-orderness and accessibility of isolated  $\text{Sn}^{4+}$  active centers to the reactants, it can only be discerned by the optimization of different synthesis variables.

Although synthesis of Sn-MCM-41 is known [8], no systematic study was reported with regard to influence of various synthesis parameters including silicon and tin sources on physicochemical properties of Sn-MCM-41. The synthesis procedure disclosed in the paper of Chaudhari et al. [8] involves the use of surfactant in the form of cetyltrimethylammonium hydroxide (CTMAOH) in combination with CTMACl. However, to produce CTMAOH from CTMACl or CTMABr, additional cost and procedural steps are involved. Moreover, the intensity of XRD pattern of MCM-41 prepared using CTMACl was found much lower than that of prepared using CTMABr [35]. As  $\text{Br}^-$  anions are more difficult to solvate and interact strongly with the cationic micelle head than  $\text{Cl}^-$  anions, the selection and use of efficient anionic species are also very important in obtaining a good quality MCM-41 material. Therefore, in present work, we have used surfactant in the form of CTMABr which is less expensive and easily available for optimizing various synthesis parameters for the preparation of good quality of Sn-MCM-41. Current work presents systematic studies on optimization of several synthesis variables such as synthesis time and the compositional variables in the starting gel, viz. molar ratios of  $\text{TMAOH/SiO}_2$ ,  $\text{CTMABr/SiO}_2$ ,  $\text{H}_2\text{O/SiO}_2$ ,  $\text{SiO}_2/\text{SnO}_2$

and silica and/or tin sources whose cause and effect relationship on the properties of Sn-MCM-41 materials. Selected Sn-MCM-41 materials prepared using different silica and tin sources were evaluated for their efficiency in Mukaiyama-aldol condensation of methyl trimethylsilyldimethyl ketene acetal and benzaldehyde under solvent-free system at 373 K.

## 2. Experimental

### 2.1. Materials

The hydrothermal syntheses of Si-MCM-41 and Sn-MCM-41 were carried out using cetyltrimethylammonium bromide, CTMABr (99%, Dishman Pharmaceutical and Chem. Ltd., Mumbai, India), tetramethylammonium hydroxide, TMAOH (aq. 25 wt.%, Loba Chemie), and distilled water. Three different silica sources, viz. (i) fumed silica (99%, Aldrich), (ii) ethyl silicate (99%, 40 wt.%  $\text{SiO}_2$ , V.P. Chemicals, Pune, India), (iii) silica sol (99%, 40 wt.%  $\text{SiO}_2$ , V.P. Chemicals, Pune, India) and three tin sources, viz. (i) tin *tert*-butoxide (99.5%, Lancaster), (ii) sodium stannate (98%, Robert Johnson) and (iii) tin tetrachloride (98%, Loba Chemie) were used in the present work.

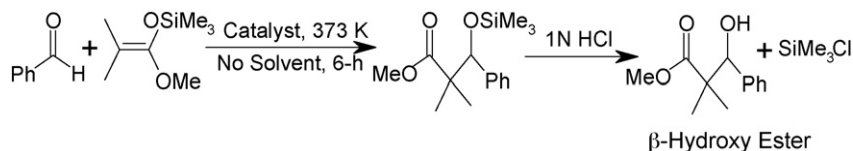
### 2.2. Hydrothermal synthesis

#### 2.2.1. Synthesis of Si-MCM-41

Purely siliceous MCM-41 was prepared by following the procedure described elsewhere [36]. The molar composition of the starting synthesis gel was:  $\text{SiO}_2:0.18\text{CTMABr}:0.25\text{TMAOH}:25\text{H}_2\text{O}$ . CTMABr was dissolved in distilled water and then added to an aqueous TMAOH solution with constant stirring. Finally, to this solution, fumed silica was added slowly with vigorous stirring. The mixture was stirred further for 2 h to obtain the starting synthesis gel. This gel was then heated in a sealed stainless steel autoclave at 383 K for 48 h. The product was recovered by filtration, washed thoroughly with distilled water and then dried at 373 K for 4 h. The removal of the template was accomplished by calcination in air at 813 K for 6 h (heating rate of  $1\text{ K min}^{-1}$ , dwell time of 2 h at 373, 473 and 623 K). This sample also was used as a substrate for the preparation of Sn-impregnated (molar  $\text{SiO}_2/\text{SnO}_2$  ratio = 250) MCM-41 by following conventional wet impregnation method. 2.55 g of calcined pre-activated Si-MCM-41 sample was added to a solution of 0.06 g  $\text{SnCl}_4\cdot 5\text{H}_2\text{O}$  in 5 g of ethanol. The mixture was then heated at 353 K with constant stirring till the sample became completely dry. The impregnated sample was then dried for 2 h at 373 K and calcined at 673 K for 6 h.

#### 2.2.2. Synthesis of Sn-MCM-41

The hydrothermal syntheses of Sn-MCM-41 were carried out using different gels with compositions  $\text{SiO}_2:w\text{SnO}_2:x\text{CTMABr}:y\text{TMAOH}:z\text{H}_2\text{O}$  where  $w$ ,  $x$ ,  $y$  and  $z$  were varied in the range of  $0.004 < w < 0.01$ ,  $0.18 < x < 0.32$ ,  $0.25 < y < 0.35$ ,  $25 < z < 45$ . Each system was subjected to identical set of synthesis conditions including downstream processing to investigate influence of individual parameter on the quality of the phase formed. In a typical synthesis of Sn-MCM-41, 10 g of fumed



Scheme 1.

silica was added slowly to 18.22 g of aqueous TMAOH solution with constant stirring. After homogenizing the mixture, 0.24 g of tin tetrachloride dissolved in 20.33 g of distilled water was added slowly with constant stirring. To this mixture, 14.66 g of CTMABr dissolved in 40 g of distilled water was added with constant stirring. The thick gel thus obtained was stirred for another 2 h. The molar composition of this starting synthesis gel was  $\text{SiO}_2:0.004\text{SnO}_2:0.24\text{CTMABr}:0.30\text{TMAOH}:25\text{H}_2\text{O}$ . This gel was then heated in a sealed stainless steel autoclave at 383 K for desired length of period. The time at which autoclave attained the 383 K temperature was taken as zeroeth hour. Since, the synthesis time is a critical variable in the formation of M41S materials [36,37], time dependant studies for the monitoring of the degree of ordering of the pore structures (structural regularity) of MCM-41 have been conducted for each system under investigation in the present studies. From such time dependant studies, the optimum synthesis period required to obtain a sample with highest peak intensities and unit cell parameter ' $a_0$ ' from this typical system was found to be 66 h. The product was recovered by filtration, washed thoroughly with distilled water and then with about 50 ml acetone. The material is then dried in air oven at 373 K for 4 h. The removal of the template was accomplished by calcination in flowing air at 813 K for 6 h (heating rate of  $1 \text{ K min}^{-1}$ , dwell time of 1 h at 373 K and 2 h at 473, 573, 623 and 723 K). Another Sn-MCM-41 sample with high tin content was prepared by following the identical procedure described above using 0.86 g tin tetrachloride while preparation of the initial gel (molar  $\text{SiO}_2/\text{SnO}_2$  ratio = 100) and optimal synthesis period was found to be 72 h.

In order to investigate the influence of individual synthesis variable such as molar TMAOH/ $\text{SiO}_2$ , CTMABr/ $\text{SiO}_2$ ,  $\text{H}_2\text{O}/\text{SiO}_2$  ratios, the type of silica sources and tin sources used in the starting gel composition on the quality of Sn-MCM-41, all other synthesis parameters such as addition sequence, molar ratios of other variables in initial reaction mixture, synthesis temperature, ratio of charged reaction mass to autoclave volume and downstream process conditions were kept constant.

### 2.3. Characterization

The X-ray diffractograms were recorded on Rigaku Miniflex (Japan) diffractometer using  $\text{Cu K}\alpha$  radiations. The diffraction data were recorded in the  $2\theta$  range of  $1.5\text{--}10^\circ$  at an interval of  $0.02^\circ$  with a scanning rate of  $1^\circ \text{ min}^{-1}$ . The morphology was examined using scanning electron microscope (JEOL-JSM-5200) after coating with Au-Pd evaporated film. The chemical compositions of the samples were determined by a combination of wet chemical methods and atomic absorption spectrometry (Varian SpectrAA 220 FS). Nitrogen adsorption and desorption

isotherms were obtained at 77 K using Omnisorp, 100 CX. Prior to the experiments, the samples were degassed under vacuum at 573 K for 10 h. The specific surface area of the sample was calculated using BET method. The pore size distribution was calculated using desorption branches of nitrogen isotherms and BJH method. Although, the BJH method is known to underestimate the pore sizes, this simple model is useful for comparison purpose. The UV–vis diffuse reflectance spectra of the samples were obtained using a Shimadzu (Model UV-2101 PC) spectrometer.

### 2.4. Catalytic reaction and products analysis

Catalytic liquid-phase Mukaiyama-aldol condensation reaction of methyltrimethyl silyl ketene acetal and benzaldehyde was performed at 373 K to produce  $\beta$ -hydroxy ester under solvent-free system. This catalytic reaction was carried out using a batch reactor at atmospheric pressure. Before the reaction, each catalyst was activated at 393 K in a vacuum oven and immediately used for the reaction under extremely dry condition. The progress of the reaction was monitored by analyzing the aldol products removed at different intervals (upto 24 h). In this reaction, to get the aldol (final product) product, the reaction was quenched by the 1N HCl solution as shown in the following reaction (Scheme 1). In a typical reaction, the mixture consisted of 10 mmol of 1-methoxy-2-methyl-1-(trimethylsilyloxy) propene, 10 mmol of benzaldehyde and 0.35 g of catalyst were stirred in a 25 ml round bottom glass flask for 24 h at 373 K. The progress of the reaction was monitored by analyzing the products at end of 3, 6, 12 and 24 h. The products were analyzed by gas chromatography (Varian, equipped with a capillary column, 20 m in length and flame ionization detector) and confirmed through authentic samples, GC–MS,  $^1\text{H NMR}$  and  $^{13}\text{C NMR}$ .

## 3. Results and discussion

Si-MCM-41 obtained from a system  $\text{SiO}_2:0.18\text{CTMABr}:0.25\text{TMAOH}:25\text{H}_2\text{O}$  exhibited well defined XRD pattern which matches well with the characteristics of hexagonal mesoporous MCM-41 phase [1]. Upon calcination, it has shown considerable increase in the intensity of low angle reflection and shifting of  $2\theta$  to higher value. Considering the XRD data and  $\text{N}_2$  sorption results, this calcined Si-MCM-41 has shown an average BJH pore diameter of the magnitude 2.36 nm, BET surface area  $1070 \text{ m}^2/\text{g}$  and 1.88 nm wall thickness. It is interesting to note that under the identical set of synthesis conditions, when tin tetrachloride ( $\text{SiO}_2/\text{SnO}_2 = 250$ ) was added to the same gel as that of used to obtain Si-MCM-41, the disordered Sn-MCM-41 was obtained. No phase transformation or improvement in

Table 1

Details of systems, their molar composition and product obtained therefrom using fumed silica and tin tetrachloride as sources of silicon and tin, respectively

System designation	Molar composition					Product by powder XRD
	SiO <sub>2</sub>	CTMABr	TMAOH	H <sub>2</sub> O	SnO <sub>2</sub>	
I	1	0.18	0.25	25	0.004	Disordered MCM-41
II	1	0.18	0.30	25	0.004	Disordered MCM-41
III	1	0.18	0.35	25	0.004	Lamellar
IV	1	0.24	0.35	25	0.004	Lamellar
V	1	0.24	0.30	25	0.004	MCM-41
VI	1	0.24	0.25	25	0.004	Disordered MCM-41
VII	1	0.32	0.30	25	0.004	Disordered MCM-41
VIII	1	0.24	0.30	35	0.004	Disordered MCM-41
IX	1	0.24	0.30	45	0.004	Disordered MCM-41

quality of MCM-41 was observed even if the synthesis period was prolonged up to 82 h. Therefore, in order to improve the quality of Sn-MCM-41, further investigations were carried out aimed at optimization of various compositional variables in the initial gel such as molar ratios of TMAOH/SiO<sub>2</sub>, CTMABr/SiO<sub>2</sub>, H<sub>2</sub>O/SiO<sub>2</sub> keeping the silica and tin sources fixed. One parameter was varied at a time keeping other synthesis variables undisturbed. The details of systems, their molar compositions and products obtained therefrom using fumed silica and tin tetrachloride as source materials are given in Table 1.

### 3.1. Optimization of gel parameters affecting the synthesis of Sn-MCM-41

The influence of concentration of the reactants on the phase quality has been investigated systematically. Keeping fixed molar ratio of SiO<sub>2</sub>/SnO<sub>2</sub> = 250, other molar ratios of TMAOH/SiO<sub>2</sub>, CTMABr/SiO<sub>2</sub>, H<sub>2</sub>O/SiO<sub>2</sub>, in the gels were varied, one at a time, to optimize the suitable gel composition and synthesis time to yield well ordered Sn-MCM-41. The influence of molar TMAOH/SiO<sub>2</sub> ratio on the quality of phase formed was investigated from systems I to III wherein, except the molar TMAOH/SiO<sub>2</sub> ratio (varied from 0.25 to 0.35), all the other parameters were kept constant. The powder XRD patterns of the phases obtained from these systems are depicted in Fig. 1. It is clearly evident from this figure that, though none of these

products are of good quality Sn-MCM-41, among these three systems slightly improved quality of Sn-MCM-41 was obtained from system II as compared to the systems I and III. In view of assessing the influence of molar TMAOH/SiO<sub>2</sub> ratio in the gel containing higher concentration of surfactant, further synthesis runs were taken keeping CTMABr/SiO<sub>2</sub> molar ratio 0.24 fixed and varied TMAOH/SiO<sub>2</sub> again the same range (from 0.25 to 0.35). It is interesting to note that the good quality of Sn-MCM-41 was obtained from System V, much better than that of obtained from system II. Thus, irrespective of molar CTMABr/SiO<sub>2</sub> ratio used in the starting gel, there exists an optimum TMAOH/SiO<sub>2</sub> ratio of 0.30, below and above which the product quality gets deteriorated. Probably, on account of lack of sufficient quantity of OH<sup>-</sup> concentration needed for digestion of silica, the system with lower concentration of TMAOH was found to lead the formation of more disordered MCM-41 structure, while a system with higher TMAOH concentration tends to yield a lamellar phase. In the present studies, the products obtained from systems III and IV became featureless after calcination. Moreover, comparing the gel composition of Si-MCM-41, it can be concluded that the formation of Sn-MCM-41 occurs when concentration of TMAOH is higher than that of Si-MCM-41.

As described above, the quality of Sn-MCM-41 was found to improve on increasing the surfactant concentration keeping molar TMAOH/SiO<sub>2</sub> ratio = 0.30 fixed. The dependence of the phase quality on the concentration of CTMABr was further investigated by increasing molar CTMABr/SiO<sub>2</sub> ratio to a value of 0.32. Thus, system VII wherein the gel with molar compositions SiO<sub>2</sub>:0.004SnO<sub>2</sub>:0.32CTMABr:0.30TMAOH:25H<sub>2</sub>O was prepared and subjected to hydrothermal treatment. Therefore, the role of concentration of CTMABr in the synthesis of Sn-MCM-41 can be very well seen from the product quality obtained from systems II, V and VII. The powder XRD patterns of as-synthesized Sn-MCM-41 samples obtained from these systems have shown in Fig. 2. It is evident from the figure that, with increase in the molar ratio of CTMABr/SiO<sub>2</sub>, the quality of Sn-MCM-41 improves, reaches to maximum and then decreases. The decrease in the quality of Sn-MCM-41 was evidenced by the reduced intensity and broadening of low angle reflection. Such drop in the quality may be partly attributed to the prohibition from growing of MCM-41 crystallite and decreased polymerization of silica by excess of

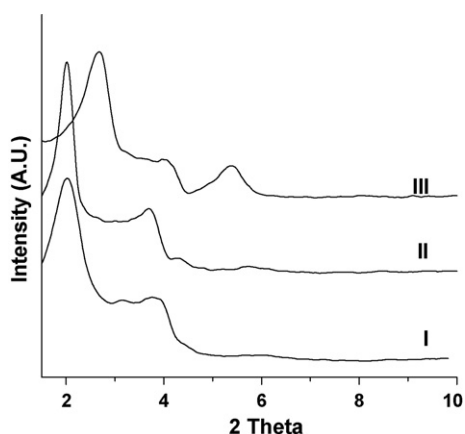


Fig. 1. Powder XRD patterns of as-synthesized phases prepared from systems with molar ratios of TMAOH/SiO<sub>2</sub>: (I) 0.25, (II) 0.30 and (III) 0.35 in the gels.

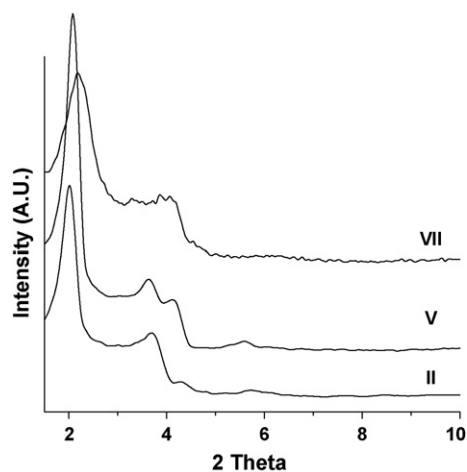


Fig. 2. Powder XRD patterns of as-synthesized Sn-MCM-41 prepared from systems with molar ratios of CTMABr/SiO<sub>2</sub>, (II) 0.18, (V) 0.24 and (VII) 0.32 in the gels.

surfactant. On summarizing the results on optimization studies for molar ratios of CTMABr/SiO<sub>2</sub> and TMAOH/SiO<sub>2</sub>, it can be concluded that, a system having gel composition SiO<sub>2</sub>:0.004SnO<sub>2</sub>:0.24CTMABr:0.30TMAOH:25H<sub>2</sub>O is the better choice for hydrothermal synthesis of good quality of Sn-MCM-41. This composition was further considered for the optimization of water concentration in the initial reaction mixture.

Since the reduction in water concentration caused the difficulty in making homogeneous gel, the gel was diluted to different extent for investigating the effect of water concentration on the quality of Sn-MCM-41. As can be seen from the compositions of systems V, VIII and IX, the molar ratio of H<sub>2</sub>O/SiO<sub>2</sub> was varied systematically from 25 to 45 keeping other parameters constant. Powder XRD patterns of the products obtained from these systems are shown in Fig. 3. With increase in the gel dilution, the quality of Sn-MCM-41 drops down as evidenced by the reduced intensity and broadening of low angle reflection. Such detrimen-

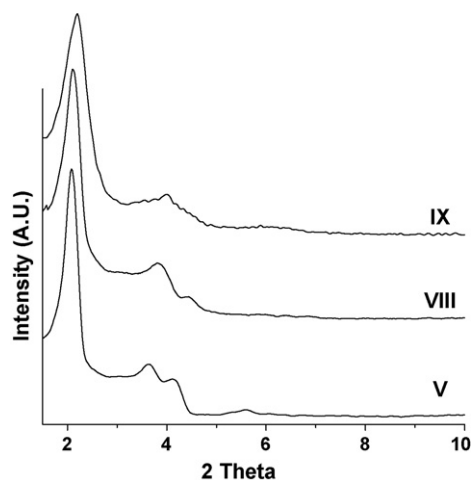


Fig. 3. Powder XRD patterns of as-synthesized Sn-MCM-41 prepared from systems with molar ratios of H<sub>2</sub>O/SiO<sub>2</sub>: (V) 25, (VIII) 35 and (IX) 45 in the gels.

tal effect may be partly attributed to the decrease in the effective concentrations of the reacting species with increase in the water content. Probably, at higher degree of dilution, prohibition from growing of MCM-41 crystallite and decreased polymerization of silica might be operative in the formation of poorer quality of Sn-MCM-41. On the basis of the results obtained from above optimization work, one can conclude that, although each synthesis variable contributes to a specific aspect of synthesis of Sn-MCM-41, there is a substantial interplay between them. Thus, keeping fixed molar ratio of SiO<sub>2</sub>/SnO<sub>2</sub> = 250, the optimum values for other crucial compositional variables in the initial gel such as molar ratios of TMAOH/SiO<sub>2</sub>, CTMABr/SiO<sub>2</sub>, H<sub>2</sub>O/SiO<sub>2</sub> were found to be 0.30, 0.24 and 25.0, respectively. The well ordered Sn-MCM-41 was obtained from this gel after undergoing the hydrothermal treatment at 383 K for 66 h.

### 3.2. Effect of silica and tin sources

As described earlier, well ordered Sn-MCM-41 (SiO<sub>2</sub>/SnO<sub>2</sub> = 250) was successfully synthesized from a gel with an optimum molar composition SiO<sub>2</sub>:0.004SnO<sub>2</sub>:0.24CTMABr:0.30TMAOH:25H<sub>2</sub>O using fumed silica and tin tetrachloride as silicon and tin sources, respectively. In order to investigate the influence of silica and/or tin source materials on the quality of Sn-MCM-41, gels with different combinations of silica and tin sources were prepared and subjected to hydrothermal treatment. Three silica and three tin sources were used in this study for the preparation Sn-MCM-41 under the identical set of synthesis conditions. Except desired silica and/or tin source, other synthesis parameters such as gel composition (same as stated above), addition sequence, synthesis temperature, ratio of charged reaction mass to autoclave volume and downstream process conditions were kept constant. The degree of ordering of the pore structure of Sn-MCM-41 was also monitored by varying the syntheses times for each system. From such time dependant studies, the optimum synthesis period required to obtain a sample with highest peak intensities and unit cell parameter 'a<sub>0</sub>' from this each system was identified. Powder XRD patterns of as-synthesized Sn-MCM-41 prepared from various combinations of silica and tin sources are depicted in Fig. 4. The quality of Sn-MCM-41 phase in terms of intensity and the position of (1 0 0) reflections was found to change with change in the source. The details regarding sample designation, the synthesis time required to obtain most ordered Sn-MCM-41 from each system, type of source combinations used, chemical analyses in terms of molar SiO<sub>2</sub>/SnO<sub>2</sub> ratio in product and XRD data for each Sn-MCM-41 are summarized in Table 2. Samples A–C form one set where silica source, viz. fumed silica was kept constant and tin sources were varied in such a way that molar SiO<sub>2</sub>/SnO<sub>2</sub> ratio in gel should remain 250. If relative intensity and sharpness of the XRD peak (*d*<sub>100</sub>) were taken as a measure of relative orderness and quality of Sn-MCM-41, it is evident from Fig. 4 that, samples A and B both were found to be more ordered and of high quality as compared to samples C. Similarly, samples A, D and E form another set where tin source, viz. tin tetrachloride was kept constant and silica sources were varied without disturbing molar SiO<sub>2</sub>/SnO<sub>2</sub> ratio in the gel. From XRD examinations,

Table 2

Sample designation, silica and tin source combination used in gel, hydrothermal synthesis period required, composition and XRD data of various Sn-MCM-41 materials

Sample code	Sources		Molar SiO <sub>2</sub> /SnO <sub>2</sub> ratio		Synthesis time (h)	XRD data	
	Silica	Tin	Gel	Product		<i>d</i> <sub>100</sub> (nm)	Unit cell parameter, <i>a</i> <sub>0</sub> (nm)
A	Fumed silica	Tin tetrachloride	250	247	66	4.24	4.89
B	Fumed silica	Tin <i>tert</i> -butoxide	250	248	66	4.30	4.96
C	Fumed silica	Sodium stannate	250	243	72	3.84	4.43
D	Silica sol	Tin tetrachloride	250	247	72	4.12	4.75
E	Ethyl silicate	Tin tetrachloride	250	246	36	4.01	4.63
F	Fumed silica	Tin tetrachloride	100	98	72	4.37	5.04

samples A and D both were found to be more ordered and of high quality as compared to sample E. Thus, among silica sources, fumed silica and silica sol were proved to be better sources when they were used in combination with tin tetrachloride. Moreover, a well ordered Sn-MCM-41 was also obtained using combination of fumed silica and tin *tert*-butoxide. It is noteworthy here that, a combination of ethyl silicate and sodium stannate sources has failed to form a well ordered Sn-MCM-41 even if the hydrothermal synthesis was allowed to last for 92 h. Unit cell parameter '*a*<sub>0</sub>' for each product was calculated using the relation  $2d_{100}/\sqrt{3}$  and is included in Table 2. It is interesting to note that, using the same source materials, synthesis period was found to increase with the increase in the tin content in the gel. It is noteworthy here that, despite the identical molar SiO<sub>2</sub>/SnO<sub>2</sub> ratio in the gel, the nature of silicon and tin sources seems to be operative in controlling the progressive development of Sn-MCM-41 phase and hence in their structural characteristics. On account of larger size of Sn<sup>4+</sup> (radius, 0.55 Å) compared with Si<sup>4+</sup> (radius, 0.26 Å) as well as to the longer bond length of Sn–O than that of Si–O [8], the Sn-MCM-41 samples containing nearly same

molar SiO<sub>2</sub>/SnO<sub>2</sub> ratio, should have shown identical values of unit cell parameters. But, in present studies, the nature of silicon and tin sources seems to be operative in controlling the growth of unit cell parameters. The variations in the XRD data caused by the change in the source materials may be associated with differences in the packing of the surfactant, the electrical double layer in the surfactant aggregate and the long-order structure [11]. Thus, at this juncture, it can be assumed that, even though, the molar SiO<sub>2</sub>/SnO<sub>2</sub> ratio in Sn-MCM-41 is nearly identical, the population of tetravalent tin responsible for expansion in hexagonal unit cell need not be necessarily same. However, with decreased molar SiO<sub>2</sub>/SnO<sub>2</sub> ratio in Sn-MCM-41, an increase in the *a*<sub>0</sub> value suggests the increase in the population of tetravalent tin that incorporated in the silicate framework of MCM-41. It is evident from Table 2 that, the population of tetravalent tin incorporated in the silicate framework of MCM-41 which can be assumed to be responsible for the expansion of unit cell follows the trend as: F > B > A > D > E > C. Sn-MCM-41 samples obtained from each system have shown lower molar SiO<sub>2</sub>/SnO<sub>2</sub> ratio in comparison with their molar SiO<sub>2</sub>/SnO<sub>2</sub> ratio in the synthesis gel.

Prior to elucidating the performance of Sn-MCM-41 catalyst in Mukaiyama-aldol condensation, further detailed characterization with regard to their texture, configuration of Sn species and morphology has been carried out using conventional techniques.

### 3.3. Textural characteristics of Sn-MCM-41

All the samples listed in Table 2 were calcined under identical programme. They have shown considerable increase in the intensity of low angle reflection and shifting of  $2\theta$  to higher values as compared to their as-synthesized forms. Surface and textural properties of these calcined samples were examined by low temperature nitrogen sorption. Nitrogen sorption isotherm of each sample exhibited a sharp and well-developed step in the relative pressure range of 0.2–0.4, characteristic of capillary condensation of nitrogen within uniform mesopores. Although, the validity of BJH method is questionable for pore diameters <5 nm, the error in the pore diameter distribution is expected to be same for very similar materials. The textural characteristics such as specific pore volume, BET surface area and average BJH pore diameter deduced from the nitrogen sorption isotherms for all these samples are summarized in Table 3. It also includes the

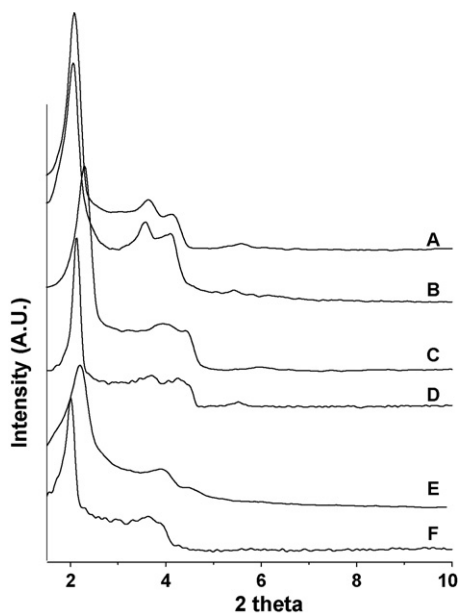


Fig. 4. Powder XRD patterns of as-synthesized Sn-MCM-41 prepared from various combinations of silica and tin sources (for sample codes please refer Table 2).

Table 3  
Textural/structural characteristics of Si- and various Sn-MCM-41

Sample designation	Total pore volume (cm <sup>3</sup> g)	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	BJH pore diameter (nm)	Wall thickness (nm)
A	0.86	1150	2.49	1.58
B	0.84	1168	2.48	1.63
C	0.71	959	2.45	1.72
D	0.79	972	2.56	1.75
E	0.90	875	3.10	2.16
F	0.83	904	3.11	1.26
Si-MCM-41	0.63	1070	2.36	1.88

magnitude of their wall thickness which is calculated by taking the difference between the unit cell parameter  $a_0$  and the average pore diameter. It can be very well seen from this table that, the textural properties changes with change tin concentration and type of source materials.

### 3.4. Configuration of Sn species

Diffuse reflectance UV–vis spectroscopy is a very sensitive probe for the detection of type and coordination state of Sn species. It also relates to the verification related to the incorporation of tin in MCM-41 structure. Fig. 5 shows the typical UV–vis diffuse reflectance spectra of calcined Sn-MCM-41 samples with varying tin content and prepared by using different combination of source materials. For comparison, the spectra of pure SnO<sub>2</sub>, tin-free Si-MCM-41 and Sn-impregnated MCM-41 are also included. It is evident from this figure that, pure SnO<sub>2</sub> and Sn-impregnated MCM-41 exhibit a broad absorption at ~280 nm which may be assigned to hexacoordinated polymeric Sn–O–Sn type species [8]. It is not surprising that, no any absorption band relevant to detection of type and coordination

state of Sn species was observed in tin-free MCM-41. Although, spectra of all the calcined Sn-MCM-41 samples reveal absorption at ~208 nm suggesting the presence of Sn<sup>4+</sup> in tetrahedral coordination in the silica framework, it is manifested by the broader character. Moreover, the intensity of a band at ~208 nm was found to increase with the increase in the tin content. We believe that site-isolated Sn in a distorted tetrahedral environment and/or in penta- or octahedral coordination sphere may be associated with such broadening character of Sn-MCM-41 spectra. Probably, the amorphous nature of the pore wall having wide range of Sn–O–Si bond angles might cause the distortion in tetrahedral environment of Sn species. Moreover, it is also likely that, on account of less crystallographic order in the pore walls, higher surface area and the larger pore dimensions, hydration of some of the Sn sites might result in the formation of Sn sites with coordination number higher than four [38]. This implies that, any differences in the catalytic behavior of these materials can be attributed to intrinsic differences in Sn siting. The presence of small absorption band at 280 ± 5 nm in sample F indicates presence of hexacoordinated polymeric Sn–O–Sn type species [8]. It is evident from Fig. 5 that, samples C–F

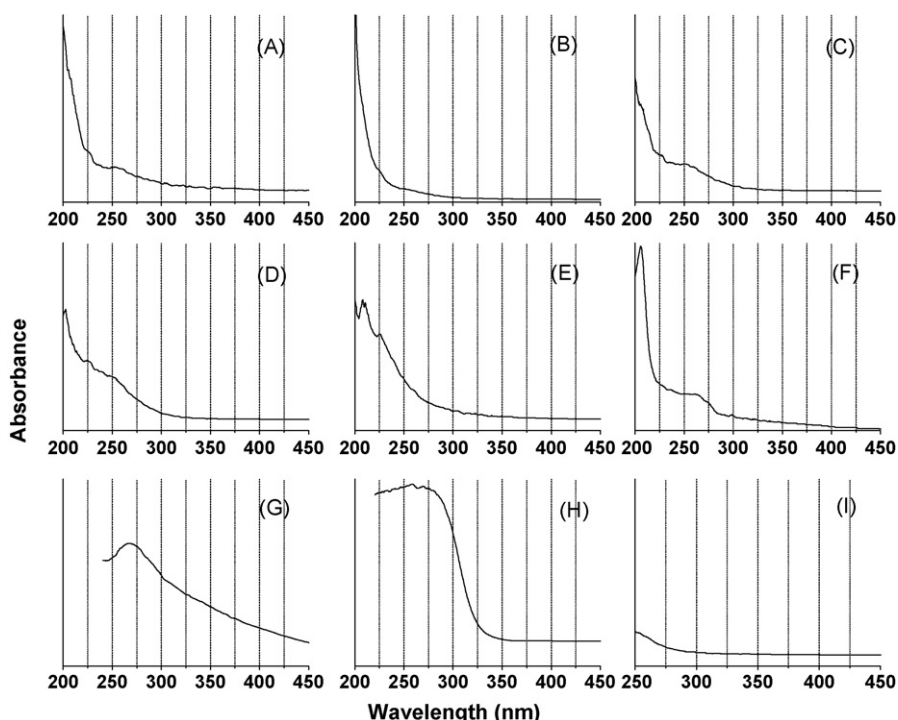


Fig. 5. Diffuse reflectance UV–vis spectra of calcined Sn-MCM-41 samples as labeled in Table 2 from A to F. (G) Sn-impregnated, (H) pure SnO<sub>2</sub>, (I) Si-MCM-41.

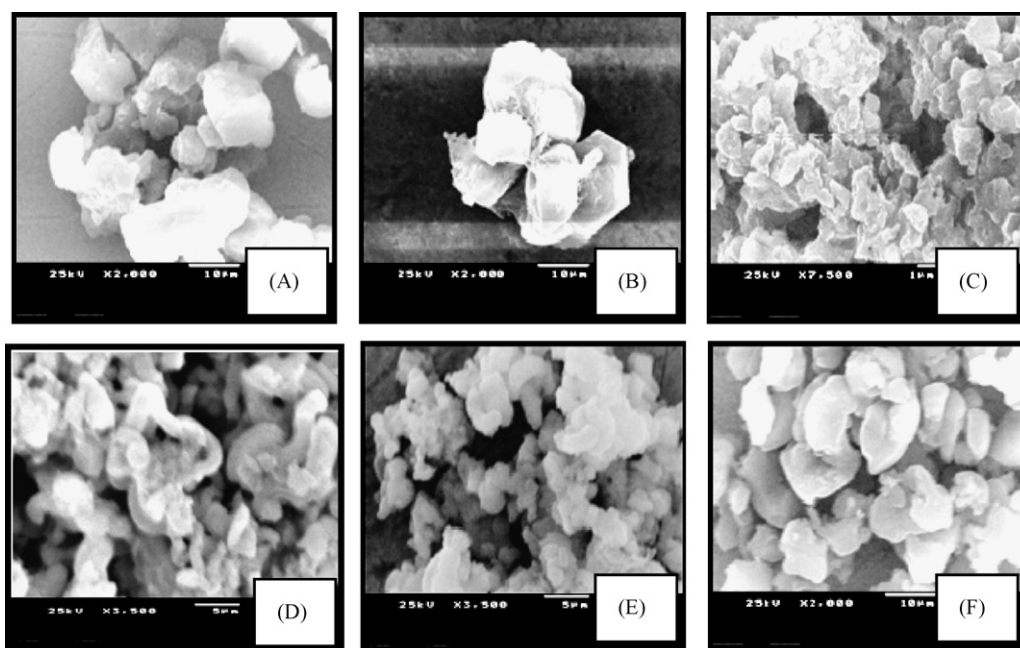


Fig. 6. SEM micrographs of Sn-MCM-41 prepared from various silica and tin sources.

have exhibited different spectral features than samples A and B. Though with minor differences, the spectral features of A and B are matching with each other with regard to non-appearance of a broad absorption at  $\sim 280$  nm and presence of absorption at  $\sim 208$  nm with more or less same intensity and broadening. Thus, when fumed silica is used in the combination of either tin tetrachloride or tin *tert*-butoxide, it was found to favor the incorporation of  $\text{Sn}^{4+}$  in tetrahedral coordination in the silica framework of Sn-MCM-41 as compared to other source combinations. In conclusion, at this juncture, the spectral features of most of the samples under investigations suggest that, the nature and concentration of tin source and/or silica source used in the present studies have influenced the not only the synthesis times but also configuration of incorporated tin species.

### 3.5. Morphology

SEM micrographs of Sn-MCM-41 samples are illustrated in Fig. 6. The morphology of Sn-MCM-41 materials was found to depend largely on the type of the silica source rather than type of tin source used in their preparation. Keeping tin tetrachloride source fixed when fumed silica was used as a silica source, irregular and indefinite shaped large agglomerates were obtained. Whereas, worm/rope like and fused particles were observed with use of silica sol and ethyl silicate, respectively. Keeping fumed silica source fixed, tin tetrachloride, tin *tert*-butoxide and sodium stannate showed some variation in their sizes with no definite shaped agglomerates. The possible cause for change in morphology with change in silica source may be the variation in the formation rate of surfactant micelles and micelle–silicate composites; hence variation in subsequent rate of silicate condensation might be responsible for giving rise to different morphology and sizes of the Sn-MCM-41 agglomerates.

On the basis of some similarities and differences in the characteristics of Sn-MCM-41 samples, four samples, viz. samples A, B, E and F were selected for evaluating their performance in solvent-free Mukaiyama-aldol condensation reaction.

### 3.6. Efficiency of Sn-MCM-41 catalysts in Mukaiyama-aldol condensation reaction

The efficiency of various catalysts in Mukaiyama-aldol condensation was examined using methyl trimethylsilyl dimethylketene acetal and benzaldehyde in solvent-free system at 373 K to produce the corresponding  $\beta$ -hydroxy ester. In present heterogeneous system, prior to conducting the Mukaiyama-type aldol reaction, all the catalysts were activated in vacuum overnight at 523 K. In this reaction, to get the aldol (final) product, the reaction was quenched by the 1N HCl solution as shown in the Scheme 1. The progress of the reaction was monitored by analyzing the aldol products removed at different time intervals (upto 24 h).

All the samples have shown the maximum conversion after 6 h. Continuing the reaction upto 24 h, only marginal increase in conversion was observed [e.g. 87% at 6 h and 88.9% at 24 h for sample A]. Therefore, for comparison purpose, the catalytic data after 3 and 6 h was considered. Invariably, the  $\beta$ -hydroxy ester selectivity was found to be 100% irrespective of the conversion levels. The activity data are therefore presented in terms of yield for desired product in Table 4.

The inactivity of Mukaiyama-aldol condensation reaction on Si-MCM-41 suggests that Sn ions are necessary for the activity. Interestingly, considering the activity data as a function of molar  $\text{SnO}_2/\text{SiO}_2$  ratio in the catalyst, the yield was found to increase with the increase in the tin content. This effect was found much pronounced when compared the activities of sample E and F. On the contrary, with nearly same difference in the



Table 4  
Catalytic activity of Si- and various Sn-MCM-41 catalysts in solvent-free Mukaiyama-aldol reaction<sup>a</sup>

Sample designation	Reaction time (h)	Yield <sup>b</sup> (%)	TON <sup>c</sup>	TOF <sup>d</sup>
A	3	81	341.77	113.92
	6	87	367.08	61.08
B	3	85	357.14	119.04
	6	91	382.35	63.72
E	3	17	72.64	24.21
	6	35	149.57	24.92
F	3	55	94.82	31.60
	6	95	146.55	24.42
Si-MCM-41	6	–	–	–

<sup>a</sup> Reaction conditions: 10 mmol of methyl trimethylsilyl dimethylketene acetal, 10 mmol of benzaldehyde, 0.35 g pre-activated catalyst, 3–6 h of reaction at 373 K under nitrogen atmosphere.

<sup>b</sup> The yield was estimated by isolation of  $\beta$ -hydroxy ester.

<sup>c</sup> Turnover number (number of molecules converted per mole of Sn).

<sup>d</sup> Turnover frequency (turnover number per hour).

tin content, sample F has shown marginal increase in the conversion when compared with conversions shown by samples A and B. Moreover, the TON (turnover number – number of molecules converted per Sn atom) decrease with increasing Sn content (sample A and F). If all the Sn ions were equally active and mono-atomically dispersed in the samples then the TON would have been same, which is not true for all the samples in present case. If all of the tin atoms were in the form of isolated tetrahedrally coordinated accessible sites, then the activity should commensurate with the Sn content. Thus, it seems that, when Sn concentration was increased from about molar SiO<sub>2</sub>/SnO<sub>2</sub> ratio of 247 to about 98, not all Sn atoms are in the form of active sites for the reaction in the present studies. Sample F has shown the presence of hexacoordinated polymeric Sn–O–Sn type species alongwith tetrahedrally coordinated Sn species. This suggests that, with the increase in tin content, either proportionate concentration of active sites decreases due to some buried sites, which are within the walls making them inaccessible to the reactants [31] and/or there is an increase in the proportion of less active Sn species among the accessible active sites [8]. However, less active/inactive/inaccessible tin species do not affect the selectivity of the catalyst. Moreover, when we compare the turnover frequency (TOF) values, the similar performance of samples E and F can also be justified.

Considering the product yields for samples A and B it can be concluded that, at such a low tin content level (0.8 wt.% Sn), an efficiency of the Sn-MCM-41 was found to be excellent. Sample B has shown 91% product yield. Solvent-free Mukaiyama-aldol-type reaction between PhCHO and silyl ketene acetal over Ti-MCM-41 containing 5.0 wt.% TiO<sub>2</sub> showed 82 mol% PhCHO conversion with 100% selectivity under the given reaction conditions [31]. Although, samples A, B and E are having more or less identical tin content, the catalytic performance of sample E was found to be very poor as compared to samples A and B. Sample B has shown the superior activity among these three catalysts. As evident from UV–vis studies, the differences

in the catalytic behavior may partly be attributed to intrinsic differences in Sn siting. Another important aspect that can be considered for explaining the differences in their catalytic efficiency is the differences in the pore regularity in these materials. An amorphous mesoporous catalyst with tetra-coordination sites shows lower activity as compared with well ordered structure, thus showing benefit of regular pore dimensions of MCM-41 [31]. Thus, the lower activity of sample E may also be due to its lower orderness, less expanded unit cell and lower surface area as evident from Fig. 4 and Tables 2 and 3. Hence, well-ordered Sn-MCM-41 with Sn species in tetrahedral coordination in the walls of its regular pores can prove as an efficient catalyst for this reaction. Moreover, when we compare the TOF (turnover frequency) values, the similar performance of samples A and B can also be justified.

Since there were no samples having the only differences in the morphologies, no meaningful conclusions can be drawn with regard to the effect of morphology on the catalytic performance of Sn-MCM-41 in the present studies. However, all these results suggest that, with further tuning of synthesis variables and reaction conditions, Sn-MCM-41 may prove a potential catalyst for the preparation of 2,2-dimethyl-3-phenyl-3-hydroxy propanoic acid methyl ester with yield as high as 100%. In conclusion, Sn-MCM-41 was found to be excellent heterogeneous catalyst for solvent-free Mukaiyama-aldol reaction in present studies. The product yield 95% has been achieved over Sn-MCM-41 catalyst containing SiO<sub>2</sub>/SnO<sub>2</sub> molar ratio of 98. The differences in the catalytic behavior of the materials under present investigation can be attributed to intrinsic differences in Sn siting and textural properties.

### 3.7. Conclusions

The suitable gel composition and the required synthesis time to obtain well ordered Sn-MCM-41 was established by optimizing the synthesis variables such as synthesis period and compositional gel components, viz. molar ratios of TMAOH/SiO<sub>2</sub>, CTMABr/SiO<sub>2</sub>, H<sub>2</sub>O/SiO<sub>2</sub>, keeping SiO<sub>2</sub>/SnO<sub>2</sub> molar ratio (250) and source materials fixed. Each synthesis variable was found to contribute to a specific aspect of synthesis of Sn-MCM-41. Well ordered Sn-MCM-41 with 0.8 wt.% Sn was obtained from the optimized gel of molar composition SiO<sub>2</sub>:0.004SnO<sub>2</sub>:0.24CTMABr:0.30TMAOH:25H<sub>2</sub>O using fumed silica and tin tetrachloride. Under this judiciously pre-optimized synthesis conditions, the different combinations of silicon sources and tin sources was found to influence the synthesis time, structural properties, tin configuration and morphology of Sn-MCM-41. Among silica sources, fumed silica and silica sol were proved to better sources when they were used in combination with tin tetrachloride. Moreover, a well ordered Sn-MCM-41 was also obtained using combination of fumed silica and tin *tert*-butoxide. A combination of ethyl silicate and sodium stannate sources has failed to the form a well ordered Sn-MCM-41 even if the hydrothermal synthesis was allowed to last for 92 h. The population of tetravalent tin incorporated in the framework which can be assumed to be responsible for the expansion of unit cell follows the trend as: F>B>A>D>E>C. The

textural properties changes with change tin concentration and type of source materials used for the synthesis of Sn-MCM-41. Sn-MCM-41 prepared using fumed silica in the combination of either tin tetrachloride or tin *tert*-butoxide has shown maximum incorporation of Sn<sup>4+</sup> in tetrahedral coordination in the silica framework of Sn-MCM-41 as compared to other source combinations. The noticeable change in morphology with change in silica source may be arising from the variation in the formation rate of surfactant micelles and micelle–silicate composites; hence variation in subsequent rate of silicate condensation.

Well-ordered Sn-MCM-41 with Sn species in tetrahedral coordination in the walls of its regular pores was found to be excellent heterogeneous catalyst for solvent-free Mukaiyama-aldol condensation between methyl trimethylsilyl dimethylketene acetal and benzaldehyde. Invariably, the  $\beta$ -hydroxy ester selectivity was found to be 100% irrespective of the conversion levels. The product, 2,2-dimethyl-3-phenyl-3-hydroxy propanoic acid methyl ester with 95% yield has been achieved over Sn-MCM-41 catalyst containing SiO<sub>2</sub>/SnO<sub>2</sub> molar ratio of 98. Sn-MCM-41 has shown remarkable activity (91% product yield) even with tin content as low as 0.8 wt.% Sn. The intrinsic differences in Sn siting, the changes in structural and textural properties are the crucial factors which were found to influence the catalytic performance of Sn-MCM-41 materials in solvent-free Mukaiyama-aldol condensation at stated conditions.

In view of the content of this article on optimization of synthesis parameters, characterization and application of Sn-MCM-41 in solvent-free Mukaiyama-aldol reaction, we strongly believe that this communication will certainly provide a base for further improvement in the quality and performance of Sn-MCM-41 and its other heteroatom containing analogues in various applications of the commercial and academic importance.

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## References

- [1] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, *Nature* 359 (1992) 710.

- [2] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, *J. Am. Chem. Soc.* 114 (1992) 10834.
- [3] K. Moller, T. Bain, *Chem. Mater.* 10 (1998) 2950.
- [4] J.Y. Ying, C.P. Mehnert, M.S. Wong, *Angew. Chem. Int. Ed.* 38 (1999) 56.
- [5] C.G. Wu, T. Bain, *Chem. Mater.* 6 (1994) 1109.
- [6] X. Fang, G.E. Fryxell, L.Q. Wnag, A.Y. Kim, J. Liu, K.M. Kemmer, *Science* 276 (1997) 923.
- [7] E. Armengol, M.L. Cano, A. Corma, H. Garcia, M.T. Nacarro, *J. Chem. Soc. Chem. Commun.* (1995) 519.
- [8] K. Chaudhari, T.K. Das, P.R. Rajmohan, K. Lazar, S. Sivasanker, A.J. Chandwadkar, *J. Catal.* 183 (1999) 281.
- [9] A. Corma, M.T. Mavaro, J. Perez-Pariente, *J. Chem. Soc. Chem. Commun.* (1994) 147.
- [10] P.T. Tanev, M. Chibwe, T.J. Pinnavaia, *Nature* 368 (1994) 321.
- [11] Y. Luo, G.L. Lu, Y.L. Guo, Y.S. Wang, *Catal. Commun.* 3 (2002) 129.
- [12] K.M. Reddy, I. Moudrakovski, A. Sayari, *J. Chem. Soc. Chem. Commun.* (1994) 1059.
- [13] A. Sayari, C. Danumah, I. Moudrakovski, *Chem. Mater.* 7 (1995) 813.
- [14] A. Sayari, I. Moudrakovski, C. Danumah, C.I. Ratcliffe, J.A. Ripmeeter, K.F. Preston, *J. Phys. Chem.* 99 (1995) 16373.
- [15] Z.Y. Yuan, S.Q. Liu, T.H. Chen, J.Z. Wang, H.X. Li, *J. Chem. Soc. Chem. Commun.* (1995) 973.
- [16] D. Zhao, D. Goldfarb, *J. Chem. Soc. Chem. Commun.* (1995) 875.
- [17] K. Narasaka, K. Soai, T. Mukaiyama, *Chem. Lett.* (1974) 1223.
- [18] T. Mukaiyama, K. Banno, K. Narasaka, *J. Am. Chem. Soc.* 96 (1974) 7503.
- [19] Y. Yamamoto, K. Maruyama, K. Matsumoto, *J. Am. Chem. Soc.* 105 (1983) 6963.
- [20] E. Nakamura, M. Shimizu, I. Kuwajima, J. Sakata, K. Yokoyama, R. Noyori, *J. Org. Chem.* 48 (1983) 932.
- [21] R. Noyori, I. Nishida, J. Sakata, *J. Am. Chem. Soc.* 105 (1983) 1598.
- [22] T. Mukaiyama, S. Kobayashi, M. Murakami, *Chem. Lett.* (1985) 447.
- [23] S. Kobayashi, M. Murakami, T. Mukaiyama, *Chem. Lett.* (1985) 1535.
- [24] M. Kawai, M. Onaka, Y. Izumi, *Bull. Chem. Soc. Jpn.* 61 (1988) 1237.
- [25] M.T. Reetz, D. Giebel, *Angew. Chem. Int. Ed.* 39 (2000) 2498.
- [26] L. Teck-Peng, L. Xu-Ran, *Tetrahedron* 55 (1999) 10789.
- [27] C.R. Brindaban, S. Manika, B. Sanjay, *Tetrahedron Lett.* 34 (1993) 1989.
- [28] R. Kumar, P. Vincent, K.V. Srinivasan, V.N. Raju, M. Sasidharan, *Chem. Commun.* (1996) 129.
- [29] R. Kumar, M. Sasidharan, *Catal. Lett.* 38 (1996) 251.
- [30] M. Sasidharan, R. Kumar, *J. Catal.* 220 (2003) 326.
- [31] R. Garro, M.T. Navarro, J. Primo, A. Corma, *J. Catal.* 233 (2005) 342.
- [32] A. Corma, L.T. Nemeth, M. Renz, S. Valencia, *Nature* 412 (2001) 423.
- [33] N.K. Mal, A.V. Ramaswamy, *J. Mol. Catal. A Chem.* 105 (1996) 149.
- [34] N. Nishiyama, M. Yamaguchi, Y. Nishiyama, Y. Egashira, K. Ueyama, *J. Non Cryst. Solids* 351 (2005) 3218.
- [35] C.-F. Cheng, D.H. Park, J. Klinowski, *J. Chem. Soc. Faraday Trans.* 93 (1997) 193.
- [36] T.R. Gaydhankar, U.S. Taralkar, R.K. Jha, P.N. Joshi, R. Kumar, *Catal. Commun.* 6 (2005) 361.
- [37] T.R. Gaydhankar, V. Samuel, P.N. Joshi, *Mater. Lett.* 60 (2006) 957.
- [38] W. Zhang, M. Fröba, J. Wang, P.T. Tanev, J. Wong, T.J. Pinnavaia, *J. Am. Chem. Soc.* 118 (1996) 9164.