

# Catalytic properties of tin-containing mesoporous molecular sieves in the selective reduction of carbonyl compounds (Meerwein–Ponndorf–Verley (MPV) reaction)

Prinson P. Samuel, S. Shylesh, A.P. Singh\*

*Inorganic and Catalysis Division, National Chemical Laboratory, Pune 411008, India*

Received 1 September 2006; received in revised form 13 October 2006; accepted 16 October 2006

Available online 20 October 2006

## Abstract

Tin-containing ordered mesoporous silica materials (Sn-OMS) were synthesized by two different routes, viz. by the direct hydrothermal method (Sn–MCM-41, Sn–MCM-48) and by the grafting method (Sn/MCM-41, Sn/MCM-48, Sn/SBA-15). The materials were characterized in detail by ICP-OES analysis, XRD, FTIR, N<sub>2</sub> adsorption–desorption, SEM and UV–vis analysis. The catalytic activity of the tin-modified mesoporous materials was ratified in the Meerwein–Ponndorf–Verley reduction of carbonyl compounds using secondary alcohols (2-butanol and 2-propanol) as hydrogen transfer agents. A comparison of catalytic activities of tin-containing mesoporous materials prepared by the two routes, dictates that tin-grafted mesoporous materials show higher catalytic activity than the tin incorporated mesoporous catalysts, even though both the materials had similar tin loadings. Among the tin-grafted catalysts, the samples prepared using the tin precursor, Me<sub>3</sub>SnCl, showed better activity than the other precursors Bu<sub>3</sub>SnCl, Ph<sub>3</sub>SnCl and Ph<sub>2</sub>SnCl<sub>2</sub> and among the mesoporous supports, Si–MCM-41 shows better catalytic results than the other supports like Si–MCM-48 and Si–SBA-15.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Mesoporous molecular sieves; MPV reduction; Cyclohexanone; 2-Butanol

## 1. Introduction

Zeolitic molecular sieves modified with metals, mainly by the isomorphous substitution or by the post synthesis grafting have attracted a great deal of research interest, because of its exceptional catalytic activity over various organic compounds [1–3]. Worldwide research interests and the increased catalytic application of these materials arise from their versatile morphological and textural properties. However, the serious diffusional limitations makes microporous zeolites less promising for reactions involving molecules having kinetic diameter greater than 6.5 Å, especially in liquid phase systems. In this sense, the fascinating discovery of mesoporous molecular sieves by Mobil researchers in 1991 triggered worldwide research interest in developing various mesoporous catalysts that can overcome the inherent diffusional limitations in the microporous zeolites [4,5]. Among the mesoporous silicates, because of the unique one-

dimensional channel walls and simple synthesis procedures, synthesis and modifications of MCM-41 (hexagonal) materials flourish larger than that of MCM-48 (cubic) and MCM-50 (lamellar) materials. Thus, the distinct features like extremely high surface area, variable pore size and presence of large number of surface silanol groups help to modify the neutral framework of these mesoporous silica materials by incorporation of hetero atoms hydrothermally or by the post synthesis grafting of the organometallic complexes/homogeneous catalysts on the active surface silanol sites [6–10]. Indeed, these metal-modified mesoporous materials are found to be useful in a variety of liquid phase reactions involving bulkier molecules, and hence received considerable attention for the last few years [11–14].

Tin-containing mesoporous molecular sieves are widely used in the chemical transformations of various bulky organic substrates [15–17]. Generally, tin-modified mesoporous materials are synthesized hydrothermally by the introduction of the required amounts of metal salt to the synthesis gel. An alternative and commonly used method to incorporate the tin species is by the post synthesis grafting procedures. However, irrespective

\* Corresponding author. Tel.: +91 20 25902583; fax: +91 20 25893761.  
E-mail address: [ap.singh@ncl.res.in](mailto:ap.singh@ncl.res.in) (A.P. Singh).

of the preparation procedures, the most important and attractive property of tin-modified molecular sieves is the Lewis acidity shown by such materials due to the presence of tetrahedrally coordinated tin sites. In fact, the creation of such Lewis acidic sites in inorganic solid supports attracts much attention due to their environmentally benign nature as they replace the soluble and corrosive strong Lewis acids used in liquid phase reactions [18]. In addition to this, in many cases, conventional Lewis acid catalysts are required in stoichiometric amounts, as the reaction products are more basic than the reactants. At this juncture, it is important to think that Meerwein–Ponndorf–Verley reduction, which is catalyzed in homogeneous system by aluminium isopropoxide in stoichiometric proportion, can be more comfortably carried out over a solid Lewis acid. Recently, considerable interest has been invested by the scientific community in the MPV reduction, as it is a mild and relatively inexpensive method for the reduction of carbonyl compounds. The potential of a broad spectrum of catalysts in the MPV reduction is well documented. In addition to the classical aluminium isopropoxide catalyst [19], catalytic applications of other isopropoxides such as zirconium(IV) isopropoxide [20,21] and lanthanide isopropoxides [22] in the MPV reaction, also have been reported. However, extensive interest have been laid on the development of heterogeneous catalysts for the MPV reaction as the homogeneous catalysts are required in stoichiometric amounts and separation of catalysts is a tedious process after the completion of the reaction. Heterogeneous catalysts for the MPV reaction include metal oxides such as magnesium oxide [23], zirconia [24,25], silica, alumina [26], etc., layered double hydroxides [27], zeolites containing different metals such as titanium [28], zirconium [29], tin [30], aluminium [31–33], etc. and hydrotalcites [34]. Heterogeneous catalysts containing grafted aluminium isopropoxide have also been reported for MPV reaction [35]. However, the activity and selectivity of MPV catalysts can be improved by introducing adequate Lewis acidity that can produce the right polarization of the carbonyl group. Thus, Sn as a heteroatom in the wall positions of mesoporous materials are ideal candidates for MPV reductions as they have higher electro negativity than Ti and more adequate for coordinating with both the reactants, viz. carbonyl compounds and alcohols (Scheme 1) [30].

In the present study, a series of tin-containing mesoporous catalysts were synthesized by the direct hydrothermal method and by the post synthesis grafting method and were then used as catalysts in the Meerwein–Ponndorf–Verley reduction of vari-

ous carbonyl compounds using 2-propanol and 2-butanol as the hydrogen transfer agents. The catalysts were characterized in detail by various physico-chemical techniques like ICP OES, XRD, FTIR,  $N_2$  adsorption–desorption isotherms, UV–vis and SEM. A series of heterogeneity tests were also performed to account for the heterogeneous nature of the Sn-modified mesoporous catalyst systems.

## 2. Experimental

### 2.1. Materials

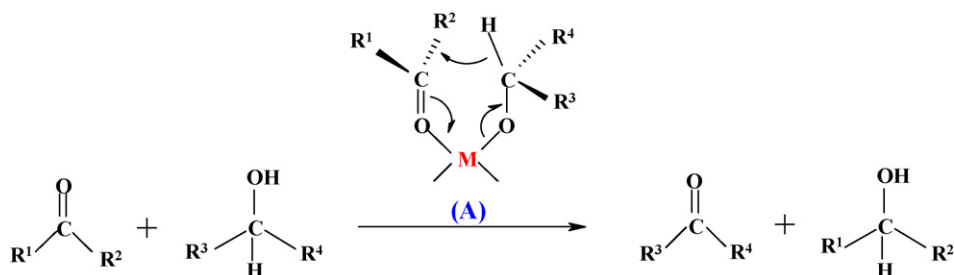
Tin-containing mesoporous silica materials were synthesized by direct hydrothermal method and post synthesis grafting method using fumed silica ( $SiO_2$ ) and tetraethyl orthosilicate (TEOS) as the silica sources and cetyl trimethyl ammonium bromide (CTMABr) and poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) (P123 copolymer) as the structure directing agents. The tin sources used were tin chloride ( $SnCl_4 \cdot 5H_2O$ ), trimethyl tin chloride ( $Me_3SnCl$ ), triphenyl tin chloride ( $Ph_3SnCl$ ), tributyl tin chloride ( $Bu_3SnCl$ ) and diphenyl tin chloride ( $Ph_2SnCl_2$ ). All the chemicals were obtained from Aldrich and were used as received.

#### 2.1.1. Synthesis of Si–MCM-41, Si–MCM-48 and Si–SBA-15

**2.1.1.1. Si–MCM-41.** Pure siliceous MCM-41 was synthesized following a previously reported procedure [10]. The synthesis was carried out by the slow addition of fumed silica to a solution of sodium hydroxide and surfactant in deionized water while vigorously stirring. After the complete addition, the pH of the gel was adjusted to 10.7 by the dropwise addition of dilute sulphuric acid. The molar composition of the final gel mixture was as follows:

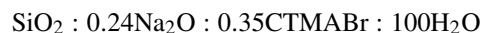


The gel was then stirred for another 2 h, transferred into a Teflon-lined autoclave and kept at  $100^\circ C$  under static conditions for 72 h. The solid material obtained was then filtered and washed well with copious amounts of water till filtrate showed a neutral pH and was then air-dried. The surfactant inside the pores of the mesoporous material was removed by calcination at  $540^\circ C$  for 6 h at a heating ramp of  $1^\circ C/min$ .



Scheme 1. MPV reduction of carbonyl compounds over Lewis acidic metal centers (M) via transition state A.

**2.1.1.2. Si–MCM-48.** The synthesis of MCM-48 was carried out by slowly adding fumed silica to a solution of sodium hydroxide in deionized water and it was vigorously stirred for 1 h. To this, a solution of the surfactant in water was added very slowly to get the final composition of gel mixture as



The gel was stirred for 2 h and heated at 150 °C in a Teflon-lined autoclave for 15 h. The resulting solid was filtered, washed and dried. The calcination of the material was carried out at 540 °C for 6 h at a temperature ramp of 1 °C/min.

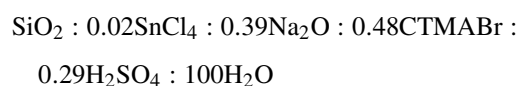
**2.1.1.3. SBA-15.** The synthesis of SBA-15 was in accordance with the procedure reported by Zhao et al. [36]. The silica source used was tetraethyl orthosilicate (TEOS) and poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) triblock copolymer (P123, Aldrich) was used as the structure directing agent. The synthesis method includes the slow addition of tetraethyl ortho silicate to a solution of block copolymer dissolved in hydrochloric acid solution under vigorous stirring. The molar composition of the gel was



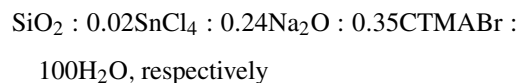
The gel was then stirred for 24 h at 40 °C, the solution was transferred to a Teflon-lined autoclave and heated at 100 °C at static condition. After cooling to room temperature, the solid product was filtered, washed, air-dried and finally calcined at 540 °C for 6 h.

### 2.1.2. Synthesis of Sn–MCM-41 and Sn–MCM-48 by direct hydrothermal method

Tin-containing MCM-41 and MCM-48 samples were prepared hydrothermally using  $\text{SnCl}_4$  as the tin source. The gel compositions of the synthesis mixture of Sn–MCM-41 and Sn–MCM-48 were



and



In detail, the gel mixtures were stirred for 6 and 10 h for Sn–MCM-41 and Sn–MCM-48, respectively, at room temperature. Then, the former gel mixture was autoclaved at 100 °C

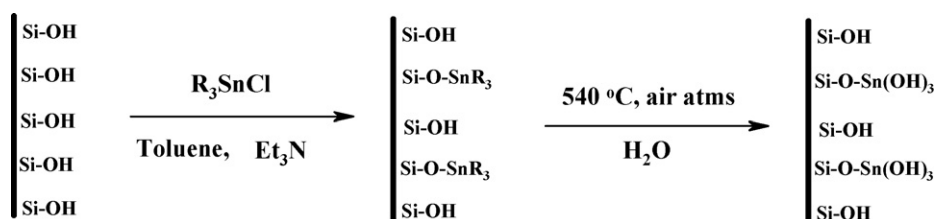
for 72 h and the later at 150 °C for 15 h. After hydrothermal treatment, the solid material obtained was filtered, washed with deionized water and dried at 100 °C for 3 h to obtain as-synthesized Sn–MCM-41 and Sn–MCM-48. The surfactant occluded inside the pores of the tin-containing mesoporous material was removed by calcination at 540 °C for 6 h.

### 2.1.3. Synthesis of Sn/OMS by grafting method

The grafting of tin over ordered mesoporous silica supports (Si–MCM-41, Si–MCM-48, Si–SBA-15) was carried out by known literature reports (Scheme 2) [17]. Tin precursors used for grafting were  $\text{Me}_3\text{SnCl}$ ,  $\text{Bu}_3\text{SnCl}$ ,  $\text{Ph}_3\text{SnCl}$  and  $\text{Ph}_2\text{SnCl}_2$ . A solution of the tin precursor in anhydrous toluene was added slowly to a suspension of the mesoporous support in toluene under stirring. After 1 h, triethylamine ( $\text{NET}_3$ ) was added and stirred for an additional 1 h to eliminate and trap the hydrochloric acid formed during Si–O–Sn bond formation. The material was then filtered, washed with toluene, dried overnight at 100 °C and finally calcined at 540 °C for 3 h in air stream, for the removal of organic components. The calcined catalysts prepared from  $\text{Me}_3\text{SnCl}$ ,  $\text{Ph}_3\text{SnCl}$ ,  $\text{Bu}_3\text{SnCl}$  and  $\text{Ph}_2\text{SnCl}_2$  are denoted as Sn/MCM-41 (Me  $x\%$ ), Sn/MCM-41 (Ph  $x\%$ ), Sn/MCM-41 (Bu  $x\%$ ) and Sn/MCM-41 (2Ph  $x\%$ ), respectively, where  $x$  represent the percentage of tin used for grafting.

## 2.2. Characterization

Powder X-ray diffraction patterns of as-synthesized and calcined mesoporous samples were recorded on a Rigaku D MAX III VC Ni-filtered Cu  $K\alpha$  radiation,  $\lambda = 1.5404 \text{ \AA}$  between 1.5 and 10° ( $2\theta$ ) with a scanning rate of 1  $\text{min}^{-1}$ . The specific surface area, total pore volume and average pore diameter were measured by  $\text{N}_2$  adsorption–desorption method using NOVA 1200 instrument (Quantachrome). The samples were activated at 180 °C for 3 h under vacuum and then the adsorption–desorption was conducted by passing nitrogen into the sample, which was kept under liquid nitrogen. Pore size distribution (PSD) was obtained by applying the BJH pore analysis applied to the desorption branch of the nitrogen adsorption–desorption isotherm. SEM micrographs of the tin-containing samples were obtained on JEOL-JSM-5200 scanning microscopy. FTIR spectra of the solid samples were taken in the range of 4000–400  $\text{cm}^{-1}$  on a Shimadzu FTIR 8201 instrument by diffuse reflectance scanning disc technique. Diffuse reflectance UV–vis spectra were recorded in the range 200–800 nm with a Shimadzu UV-2101 PC spectrometer equipped with a diffuse reflectance attachment, using  $\text{BaSO}_4$  as the reference.



Scheme 2. Grafting of tin precursors over mesoporous silica supports.

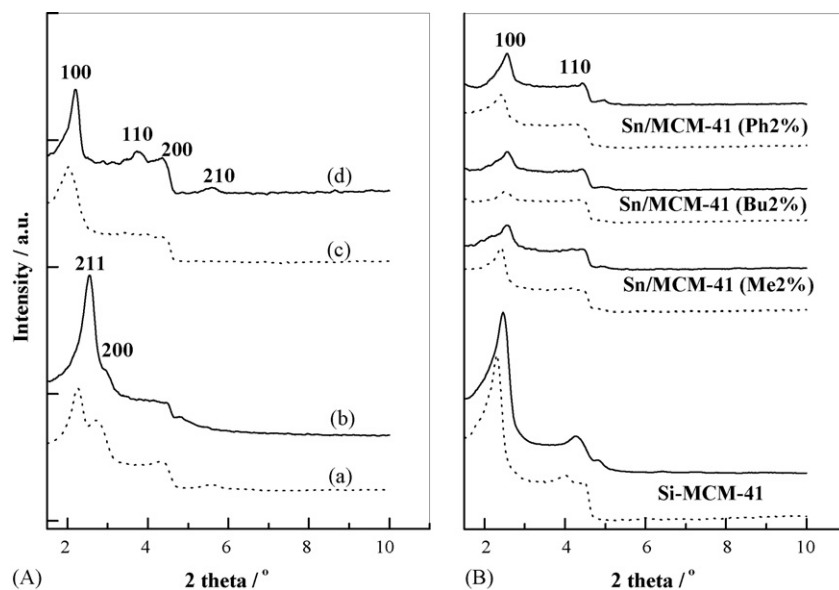


Fig. 1. XRD patterns of Sn-containing mesoporous samples—(A) by hydrothermal method: (a and b) Sn–MCM-48 and (c and d) Sn–MCM-41; (B) by grafting method. Dotted lines show as-synthesized samples and solid lines show calcined samples.

### 2.3. Catalytic reaction

The liquid phase catalytic reduction of carbonyl compounds was performed in a 10 ml double-necked round bottom flask fitted with a reflux condenser, using 2-butanol and 2-propanol as the hydrogen transfer agents. In a typical reaction, 1 mmol of carbonyl compound and 50 mmol of the reductant (2-propanol or 2-butanol) were added to 0.1 g of catalyst and was heated at a constant temperature (85 °C for 2-propanol and 100 °C for 2-butanol) under stirring. After reactions, the reaction mixture was cooled to room conditions and the catalyst was separated from the reaction mixture by centrifugation. The products were analyzed on a gas chromatograph (HP 6890) equipped with a flame ionization detector (FID) and a capillary column (5  $\mu$ m cross-linked methyl silicone gum, 0.2 mm  $\times$  50 m) and were further confirmed by GC–MS (Shimadzu 2000 A) and by authentic samples.

## 3. Results and discussion

### 3.1. X-ray diffraction

The XRD patterns of tin-containing mesoporous materials synthesized hydrothermally, are shown in Fig. 1A. X-ray diffractograms of the as synthesized and calcined Sn–MCM-41 catalysts were characterized by four distinct Bragg reflexes at low angles indexed to (1 0 0), (1 1 0), (2 0 0) and (2 1 0) representative of ordered materials with hexagonal arrangement of mesopores (Fig. 1A(c) and (d)). Meanwhile, the XRD patterns of Sn–MCM-48 materials are characterized by (2 1 1) and (2 0 0) reflections, characteristic for cubic structure (Fig. 1A(a) and (b)) and the unit cell parameter values ( $a_0$ ), calculated from the equations  $a_0 = 2d_{100}/\sqrt{3}$  (for MCM-41) and  $a_0 = d_{211}\sqrt{6}$  (for MCM-48), are shown in Table 1. Compared to the silica polymorph, tin substituted mesoporous materials show an increase in

Table 1  
Characteristics of tin-containing mesoporous materials

Sample	Sn <sup>a</sup> (%)	$a_0^b$ (Å)	$S_{\text{BET}}$ (m <sup>2</sup> g <sup>-1</sup> )	$V_p^c$ (cm <sup>3</sup> g <sup>-1</sup> )	$D_p^d$ (Å)
Si–MCM-41	–	40.49	845	0.68	32.27
Sn–MCM-41	2.3	41.47	758	0.49	24.6
Sn–MCM-48	2.8	43.60	1125	0.87	24.7
Sn/MCM-41 (Me 2%)	1.4	39.87	722	0.76	21.8
Sn/MCM-41 (Ph 2%)	0.8	39.86	680	0.46	22.3
Sn/MCM-41 (Bu 2%)	0.7	39.84	654	0.39	22.2
Sn/MCM-41 (2Ph 2%)	1.1	39.78	650	n.d.	n.d.
Sn/MCM-48 (Me 2%)	1.5	34.25	766	n.d.	n.d.
Sn/SBA-15 (Me 2%)	0.85	85.42	724	n.d.	n.d.
Sn/Silica gel (Me 2%)	0.90	–	355	n.d.	n.d.

<sup>a</sup> Determined by ICP analysis.

<sup>b</sup> Unit cell parameter:  $a_0 = 2d_{100}/\sqrt{3}$  (MCM-41, SBA-15) and  $a_0 = d_{211}\sqrt{6}$  (MCM-48).

<sup>c</sup>  $V_p$  = pore volume.

<sup>d</sup>  $D_p$  = pore diameter, n.d. = not determined.

the  $d_{100}$  values and thereby an increase in the unit cell size. This increase can be taken as an indication for the incorporation of tin in the molecular sieve framework, since the Sn–O bond distance is longer than the Si–O bond distance [37,38]. The XRD patterns of the tin-grafted mesoporous molecular sieves are given in Fig. 1B. Compared to Si–MCM-41, tin-grafted Sn/MCM-41 samples show a gradual decrease in the intensity of the characteristic  $d_{100}$  peak with a slight peak broadening and a gradual loss in the long range ordering. The decrease in intensity of the  $d_{100}$  peak and long range ordered peaks is a common phenomenon observed in mesoporous materials, during post synthesis modifications, and are attributed to the partial structural collapse of the mesoporous structure or to the flexibility induced in the silica framework due to the strain generated from the grafted species. Besides, it is interesting to note that the changes in peak intensity depend on the precursor used for the grafting reactions. For instance the structural disordering was found to be the least for the  $\text{Me}_3\text{SnCl}$ -grafted samples than the  $\text{Ph}_3\text{SnCl}$  and  $\text{Bu}_3\text{SnCl}$ -grafted samples. This result explains the less steric hindrance experienced by  $\text{Me}_3\text{SnCl}$  inside the flexible channel walls of MCM-41 than the bulkier  $\text{Bu}_3\text{SnCl}$  and  $\text{Ph}_3\text{SnCl}$  precursors. Furthermore, no bands characteristic for crystalline  $\text{SnO}_2$  phase is observed in both of the preparation methods (direct hydrothermal synthesis and grafting) in the wide-angle X-ray scattering (WAXS) and hence assumed that tin exists in a dispersed state on the support surfaces.

### 3.2. Nitrogen adsorption–desorption studies

The nitrogen adsorption–desorption results of tin-containing mesoporous samples and their corresponding pore size distribution curves are plotted in Fig. 2.  $\text{N}_2$  adsorption–desorption isotherms of all samples show Type IV isotherms, with completely reversible nature, characteristic of solids with uniformly sized mesopores according to the IUPAC classification [10]. The surface area, average pore diameter, pore volume and

the wall thickness observed for the tin-containing mesoporous materials are summarized in Table 1. The surface area of the catalysts determined by the BET method shows that the support Si–MCM-41 show a specific surface area of  $845 \text{ m}^2 \text{ g}^{-1}$  and after the grafting reactions with tin precursors the surface area get decreased. The decrease in surface area after post synthesis grafting reactions are expected, since the bulkier organic moieties inside the pore channels occupy a large area of the void space. However, after calcination, the surface area of the Sn/MCM-41 catalyst gets increased and restores to 75–85% of the support surface area, due to the removal of the organic groups. It can be seen that the surface area recovered by different catalyst samples are different, because grafting of the tin precursor will cause the structural disorder of the material to some extent depending on the strain caused by the bulkness of the organic groups. So depending on chain length of the tin precursor, the textural features of the material get varied. Further the extent of structural disordering is directly related to the nature of the tin precursor and the bulkier phenyl and butyl groups disordered the structure of the material more than the smaller methyl groups. Thus, the bulkier the organic groups in the tin precursor, the more will be the structural disorder and hence lower the surface area. The pore size distribution (PSD) curves obtained from the adsorption data shows sharp unimodal peaks at 24.6, 24.7, 21.8, 22.3 and 22.2 Å for the Sn–MCM-41, Sn–MCM-48, Sn/MCM-41 (Me 2%), Sn/MCM-41 (Bu 2%) and Sn/MCM-41 (Ph 2%) samples, respectively, indicating that the materials possess uniform pore dimensions.

### 3.3. Scanning electron microscopy

The particle size and morphology of Sn/MCM-41 samples were determined by the SEM analysis and are shown in Fig. 3. The morphology of the materials is characteristic for metal-modified mesoporous materials reported and consists of small particles of 0.6–1.5  $\mu\text{m}$  diameter [39]. However, the micro-

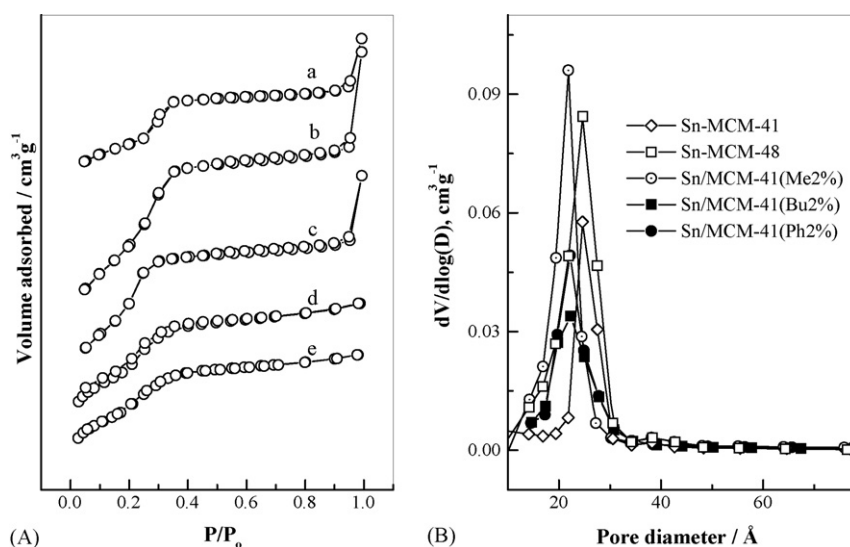


Fig. 2. (A)  $\text{N}_2$  adsorption–desorption isotherms of (a) Sn–MCM-41, (b) Sn–MCM-48, (c) Sn/MCM-41 (Me 2%), (d) Sn/MCM-41 (Ph 2%), and (e) Sn/MCM-41 (Bu 2%); (B) pore size distribution curves.

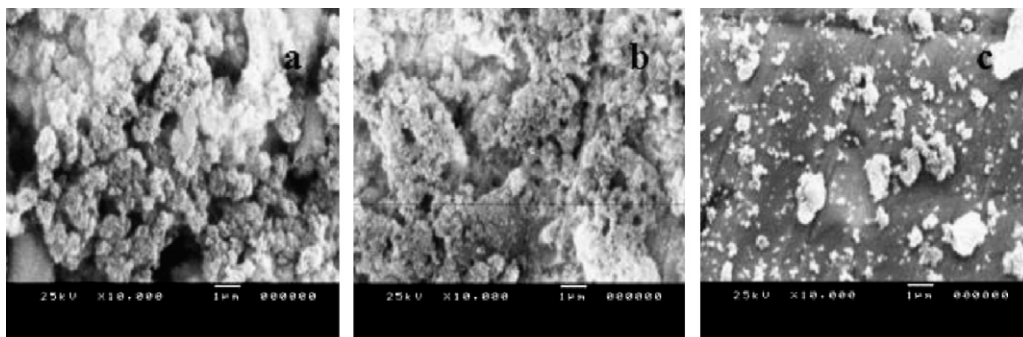


Fig. 3. SEM images of tin-containing mesoporous materials: (a) Sn/MCM-41 (Me 2%), (b) Sn/MCM-41 (Ph 2%) and (c) Sn/MCM-41 (Bu 2%).

graphs clearly show different morphologies for each type of tin-grafted samples and the reason for this relates to the kind of modifications and strain exerted inside the pores. Different degrees of strain exerted inside the pores of the mesoporous materials by different tin precursors leads to the structural disordering of the materials at different levels. In addition to this, dissimilar consumption of internal silanols by the tin precursors also triggers structural modifications in unlike ways. In short, nature and size of tin precursors change the morphological patterns of the MCM-41 sample.

### 3.4. FTIR spectroscopy

The amorphous nature of the walls of the mesoporous silica materials and the presence of the hydrogen bonded hydroxyl groups are evidenced from the IR spectrum of the tin-containing mesoporous samples (Fig. 4). The band observed in the range of  $850\text{--}770\text{ cm}^{-1}$  accounts for the symmetric stretching vibrations of the Si–O–Si bonds, and its increased intensity is an inference for a higher concentration of the siloxane groups while the band at  $1090\text{ cm}^{-1}$  is assigned to the asymmetric (Si–O–Si) vibrations. In the hydroxyl region ( $3200\text{--}3600\text{ cm}^{-1}$ ), a very broad

IR absorption band centered at  $\sim 3500\text{ cm}^{-1}$  is ascribed to the silanol groups occurring at internal sites with strong hydrogen bonded interactions as in the case of zeolites [39]. The intensity of these bands remains almost same in the case of molecular sieves obtained by direct hydrothermal method while the intensity of the silanol groups gets decreased after the grafting reactions, which shows the active participation of the surface silanols in the bond formation with the tin precursor. In detail, for Sn–MCM-41 and Sn–MCM-48 samples, intense bands are visible in the range  $980\text{--}950\text{ cm}^{-1}$  region. Even though the  $960\text{ cm}^{-1}$  band is attributed for the  $\nu_{\text{as}}(\text{Si-O-M})$  vibrations of the molecular sieves, they can also arise due to the presence of  $\nu(\text{Si-OH})$  vibrations of the silica framework and hence the band in the  $960\text{ cm}^{-1}$  region cannot be taken as a solid proof for the incorporation of tin in the framework of Sn–MCM-41 samples. However, the shifting of this band to higher wave number and the corresponding shift of the  $\nu_{\text{as}}(\text{Si-O-Si})$  band to lower wave number can be taken as an indication for the presence of tin in the framework positions of the Si–MCM-41 (48) samples [40,41]. Further, the successful grafting of the tin precursors were evidenced from the presence of sharp peaks observed in the  $2950\text{--}2850\text{ cm}^{-1}$  region which are usually assigned for the

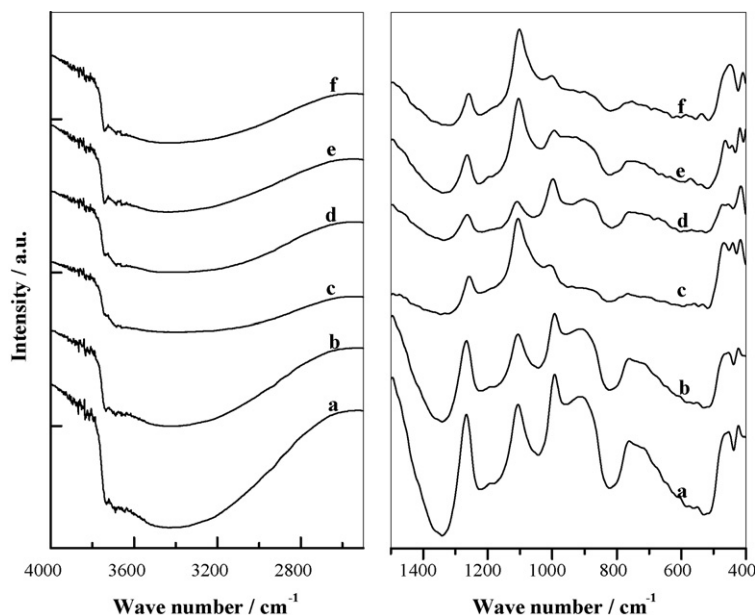


Fig. 4. FTIR spectra of (a) Si–MCM-41, (b) Sn/MCM-41 (Me 2%), (c) Sn/MCM-41 (Ph 2%), (d) Sn/MCM-41 (Bu 2%), (e) Sn–MCM-41 and (f) Sn–MCM-48.

C–H stretching and bending vibrations (figure not shown) [38]. After calcination, all the bands belonging to the organic groups had disappeared with a corresponding increase in the intensity of the Si–OH groups. These results show the removal of the bulkier organic groups from the pores of mesoporous support after calcination.

### 3.5. Diffuse reflectance UV–vis spectroscopy

In order to deduce the nature of tin species formed on MCM-41 framework, DRUV–vis measurements were performed as it generally provides valuable information about the co-ordination environment of the metal species in various molecular sieves. The UV–vis spectra of tin-containing catalysts prepared by direct methods and post synthesis grafting methods are shown in Fig. 5. For comparison, the spectrum of pure SnO<sub>2</sub> is also shown in Fig. 5A(a). Generally, tetrahedrally coordinated tin shows an adsorption band at ~220 nm while hexacoordinated tin shows bands at ~280 nm [42]. The UV–vis spectra of Sn–MCM-41 and Sn–MCM-48 show a single, sharp absorption band at 220 nm, proving the isomorphous substitution of tin in the [SiO<sub>4</sub>]<sup>4-</sup> frame work as tetrahedral species. The grafted calcined catalysts also show a sharp absorption band near 220 nm and a very weak band near 280 nm, indicating that in post synthesis grafting methods tin resides also as higher coordinated species. However, the presence of 260–280 nm band is more relevant for the Sn/MCM-41 (Ph 2%) and Sn/MCM-41 (Bu 2%) samples than the Sn/MCM-41 (Me 2%) sample. Thus, it can be concluded that tin is tetrahedrally coordinated in case of hydrothermally synthesized Sn–MCM-41 and Sn–MCM-48 catalysts while the grafted calcined catalysts show the presence of trace amounts of higher coordinated tin species also. Moreover, a comparison with pure SnO<sub>2</sub> rules out the formation of aggregated tin oxide species over the mesoporous support due to the absence of absorption band above 280 nm.

Table 2

MPV reduction of cyclohexanone over Sn-containing mesoporous catalysts

Catalyst	Conversion of cyclohexanone (mol%)	
	2-Propanol	2-Butanol
Si–MCM-41	0	0
Sn–MCM-41	8	42
Sn–MCM-48	6.5	17
Sn/MCM-41 (Me 2%)	23	82
Sn/MCM-41 (Me 2%) <sup>a</sup>	20	75
Sn/MCM-41 (Ph 2%)	10	32
Sn/MCM-41 (Bu 2%)	20	41
Sn/MCM-41 (2Ph 2%)	15	40
SnCl <sub>4</sub> ·5H <sub>2</sub> O	3	9
SnO <sub>2</sub>	2	5

Reaction conditions: substrate, 1 mmol; 2-butanol/2-propanol, 50 mmol; T, 100 °C (2-butanol) and 85 °C (2-propanol); t, 12 h; catalyst weight, 100 mg. Selectivity for cyclohexanol in all cases is 100%.

<sup>a</sup> After third run.

### 3.6. Catalytic MPV reduction of carbonyl compounds

The MPV reduction of cyclohexanone over different hydrothermally synthesized and grafted tin catalysts was performed using 2-propanol and 2-butanol as hydrogen donors and the results are summarized in Table 2. Even though, the hydrothermally synthesized catalysts contain more amount of tin, the mesoporous catalysts obtained by post synthesis method show more activity in the reduction of cyclohexanone. The reason for this behaviour relates to the more accessible active tin sites in the grafted catalysts than in the hydrothermally synthesized catalysts, where a large proportion of tin atoms are buried inside the pore walls [17]. It can be seen that, the conversion of cyclohexanone over different grafted samples are varying, and this activity difference shown by the tin-containing mesoporous catalysts prepared from various tin precursors can be related to different reasons, viz. percentage of tin loading, metal distri-

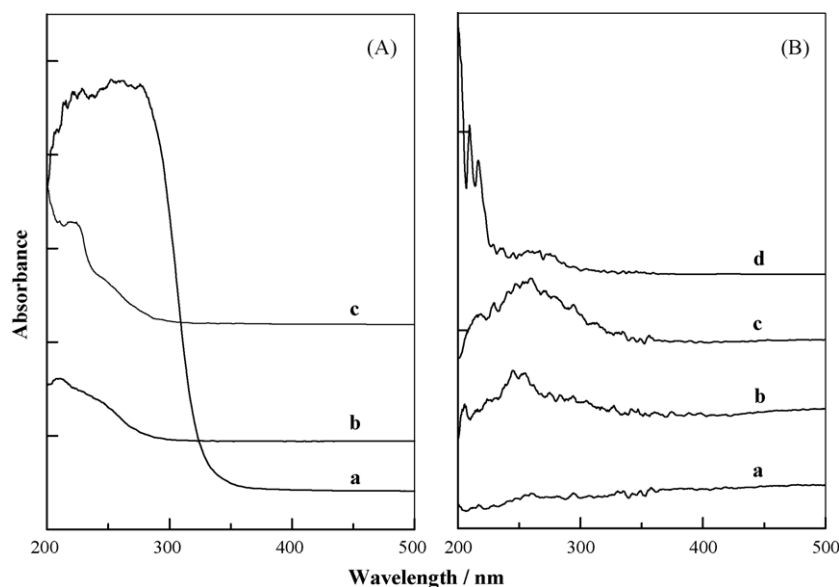


Fig. 5. UV–vis spectra of (A) hydrothermally synthesized tin catalysts: (a) SnO<sub>2</sub>, (b) Sn–MCM-41 and (c) Sn–MCM-48; (B) grafted calcined catalysts: (a) Si–MCM-41, (b) Sn/MCM-41 (Me 2%), (c) Sn/MCM-41 (Ph 2%) and (d) Sn/MCM-41 (Bu 2%).

bution, coordination environment of tin, morphology and the mesopore structural ordering. ICP-OES analysis shows maximum loading of tin in the Sn/MCM-41 (Me 2%) catalyst and it shows maximum activity. The other grafted catalysts, Sn/MCM-41 (Ph 2%), Sn/MCM-41 (Bu 2%) and Sn/MCM-41 (2Ph 2%) showed only moderate results as the percentage of grafting in these catalysts are less. Further, from spectroscopic studies it was observed that the phenyl and butyl tin precursor-grafted mesoporous samples contain octahedrally coordinated tin species and these sites are inactive in MPV reduction reactions. Hence, the greater percentage of tin as well as tetrahedrally coordinated tin sites in Sn/MCM-41 (Me 2%) relates to the better conversion than Sn/MCM-41 (Bu 2%) and Sn/MCM-41 (Ph 2%) samples. The present results shows that the nature of metal precursor has a prime role in the percentage of metal loading, metal distribution as well as the overall mesoporous structural ordering and hence in the catalytic activity. In short, even though, final catalyst samples obtained after grafting and calcination are almost similar in their chemistry, they are not same in their structural and textural features, as demonstrated by various characterization techniques and this leads to difference in their catalytic activity. The homogenous  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{SnO}_2$  catalysts show only negligible conversion of cyclohexanone in the presence of both the hydrogen donors, viz. 2-propanol and 2-butanol. These results point out that the enhanced activity of the tin-grafted mesoporous catalysts may not arise due to leached metal species and in turn shows that, tetrahedral tin sites are the active catalytic sites. Hence, the effect of molar ratio between the substrate and hydrogen donor, effect of metal loading and the influence of different supports were evaluated with the grafted catalysts.

Effect of molar ratio between the substrate and hydrogen donor, in the MPV reduction of cyclohexanone using 2-butanol is summarized in Table 3. It was observed that, higher the amount of 2-butanol lesser was the conversion and maximum conversion was obtained at a ratio of 1:50 between cyclohexanone and 2-butanol. A possible explanation is that the excess amount of alcohol may interfere in the coordination of substrate with the Lewis acid tin sites and thereby retard the polarization of the carbonyl group of the substrate. But, below 1:50 molar ratios the conversions are less and at 1:25 ratio, the reaction mixture is viscous. Hence, the optimum molar ratio between the substrate and hydrogen donor, in the MPV reduction of cyclohexanone over tin-containing mesoporous molecular sieves, was selected as 1:50. Influence of reaction time on cyclohexanone conversion

Table 3  
Effect of molar ratio in the MPV reduction of cyclohexanone

Cyclohexanone to alcohol molar ratio	Conversion of cyclohexanone (mol%)	
	2-Propanol	2-Butanol
1:25	20	76
1:50	23	82
1:100	16	47
1:200	10	17
1:300	8	9

Reaction conditions:  $T$ , 100 °C (2-butanol) and 85 °C (2-propanol);  $t$ , 12 h; catalyst weight (Sn/MCM-41 (Me 2%)), 100 mg. Selectivity for cyclohexanol is 100% in all cases.

Table 4  
Effect of tin loading on MCM-41 in the MPV reduction of cyclohexanone

Catalyst	Conversion of cyclohexanone (mol%)	
	2-Propanol	2-Butanol
Si-MCM-41	0	0
Sn/MCM-41 (Me 2%)	23	82
Sn/MCM-41 (Me 5%)	33	88
Sn/MCM-41 (Me 10%)	50	100

Reaction conditions: substrate, 1 mmol; 2-butanol/2-propanol, 50 mmol;  $T$ , 100 °C (2-butanol) and 85 °C (2-propanol);  $t$ , 12 h; catalyst weight, 100 mg. Selectivity for cyclohexanol in all cases is 100%.

over Sn/MCM-41 (Me 2%) catalyst showed that the conversion increased steadily with time and reached 44%, using 2-propanol, while with 2-butanol the conversion reached up to 100%, after 24 h. These results suggest that 2-butanol was the appropriate hydrogen donor than 2-propanol in the MPV reduction of cyclohexanone over tin-containing mesoporous molecular sieves and the results are in well accordance with the observation of Corma et al. over Sn-beta catalysts [30]. Effect of tin loading in the MPV reduction of cyclohexanone with 2-butanol and 2-propanol is given in Table 4. In order to achieve this, MCM-41 support was loaded with 2%, 5% and 10% tin using  $\text{Me}_3\text{SnCl}$  as the tin precursor and was used as catalysts in the reduction reaction of cyclohexanone. As expected, the conversion increased steadily with the percentage of tin loading and with 2-propanol, Sn/MCM-41 (Me 10%) showed a conversion of 50%, while 2-butanol shows complete cyclohexanone conversion after 12 h reaction time.

In order to understand, how the support material influences the conversion of cyclohexanone in the MPV reduction, we loaded 2 wt.% of tin over different mesoporous support materials like Si-MCM-41, Si-MCM-48, Si-SBA-15 and an amorphous silica gel. The effect of support on the conversion and selectivity observed for cyclohexanone to cyclohexanol transformation is summarized in Table 5. Tin-containing mesoporous materials showed better conversion than the silica gel-supported tin catalyst and the catalytic activity follows the order MCM-41 > MCM-48 > SBA-15 > silica gel. These results suggest that the ordered pore nature and high content of active Sn sites in mesoporous materials enhance the reduction reactions than the conventional silica gel sample and the comparatively lower conversion observed over Sn/SBA-15 may relate to the lesser amount of tin-grafted over the SBA-15 support and further works are needed to probe whether the micropores present in

Table 5  
Influence of support in the MPV reduction of cyclohexanone using 2-butanol as the hydrogen transfer agent

Catalyst	Conversion (mol%)
Sn/MCM-41 (Me 2%)	82
Sn/MCM-48 (Me 2%)	78
Sn/SBA-15 (Me 2%)	66
Sn/silica gel (Me 2%)	56

Reaction conditions: substrate, 1 mmol; 2-butanol, 50 mmol;  $T$ , 100 °C;  $t$ , 12 h, catalyst weight, 100 mg. Selectivity for cyclohexanol is 100% in all cases.



the SBA-15 sample had any negative effect in the reduction reactions.

On the basis of the above observations Sn/MCM-41 (Me 2%) seems to be the best catalyst and hence the activity of this catalyst was probed in the MPV reduction of other carbonyl compounds, viz. benzaldehyde, 2-methylcyclohexanone, 3-methylcyclohexanone, 4-methylcyclohexanone, 3-methylcyclopentanone, cyclopentanone, cycloheptanone and 2-adamantanone, and the results are summarized in Table 6. The substituted cyclohexanones are found to show only lesser conversion than cyclohexanone under similar reaction conditions and the reason for this is attributed to the fact that, the alkyl substituents in the ring induces steric hindrance near the active tin

sites in the transition state of the reaction. Substituted cyclopentanone also shows lesser conversion than cyclopentanone and the above said theory of transition state limitation is applicable in this case too. However, in the case of all the above-mentioned ring substituted cyclic ketones, selectivity towards the *trans* product is higher than the *cis* isomer and the *trans:cis* ratio is furnished in Table 6.

### 3.7. Heterogeneity tests

In order to verify whether the observed catalytic activity arises due to heterogeneous catalysis, a series of leaching experiments were performed. As a first method, the catalyst was reused under similar experimental conditions, but after washing the catalyst with copious amounts of isopropanol and drying at 200 °C for 6 h. Recycling studies shows that the catalysts are recyclable without any loss in catalytic activity even after the third run (Table 2). Secondly, the catalyst was removed from the reaction mixture after 3 h run and the filtrate was monitored for further reactions. Analysis of the filtrate even after 12 h showed that the conversion was not increased after catalyst removal. These two results confirm the heterogeneity of the tin-containing mesoporous materials and hence are excellent heterogeneous catalysts for Meerwein–Ponndorf–Verley reduction reactions.

## 4. Conclusions

In short, the surface properties and catalytic activity differences of a series of tin-containing mesoporous catalysts prepared by grafting method were compared with those prepared by direct hydrothermal method in the MPV reduction of carbonyl compounds. Spectroscopic studies confirm the major formation of tetrahedral tin sites on both the grafted and hydrothermally synthesized tin catalysts. Tin-containing mesoporous catalysts showed excellent catalytic activity in the Meerwein–Ponndorf–Verley reduction of various carbonyl compounds and the better activity of the tin-grafted catalysts than the hydrothermally synthesized catalysts is attributed to the presence of well-exposed catalytic sites. Heterogeneity studies proved that tin-containing mesoporous catalysts are highly stable under reaction conditions and hence serves as effective catalysts for the Meerwein–Ponndorf–Verley reduction of carbonyl compounds.

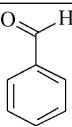
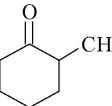
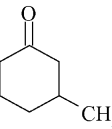
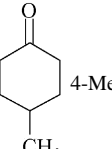
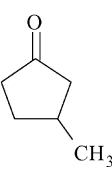
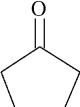
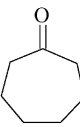
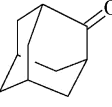
## Acknowledgements

The authors are grateful to Dr. Shubhangi, Dr. Bhelekar, Mr. R.K. Jha and Miss. Violet Samuel for their assistance with the IR, SEM, surface area analysis and XRD measurements, respectively. PPS thanks task force project funded by CSIR (P23-CMM0005B) for financial assistance and SS thanks CSIR, India for a senior research fellowship.

## References

- [1] A. Tuel, Y.B. Taarit, Zeolites 14 (1994) 18.
- [2] K.R. Reddy, A.V. Ramaswamy, P. Ratnaswamy, J. Catal. 143 (1993) 275.
- [3] R. Joseph, M. Sasidharan, R. Kumar, A. Sudalai, T. Ravindranathan, J. Chem. Soc. Chem. Commun. (1995) 1341.

Table 6  
MPV reduction of different substrates over Sn/MCM-41 (Me 2%) catalyst

Substrate	Conversion	Selectivity
 Benzaldehyde	19	100
 2-Methylcyclohexanone	38	71:29 <sup>a</sup>
 3-Methylcyclohexanone	30	79:21 <sup>a</sup>
 4-Methylcyclohexanone	28	97:3 <sup>a</sup>
 3-Methylcyclopentanone	18	68:32 <sup>a</sup>
 Cyclopentanone	20	100
 Cycloheptanone	27	100
 2-Adamantanone	25	100

Reaction conditions: substrate, 1 mmol; 2-butanol, 50 mmol; catalyst weight, 10 wt.% of substrate; *T*, 100 °C; *t*, 20 h.

<sup>a</sup> Selectivity (*trans:cis*) ratio of the product.

- [4] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, *Nature* 359 (1992) 710.
- [5] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olsen, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, *J. Am. Chem. Soc.* 114 (1992) 10834.
- [6] S. Gontier, A. Tuel, *Micropor. Mater.* 5 (1995) 161.
- [7] S. Lim, G.L. Haller, *Appl. Catal. A* 188 (1999) 277.
- [8] M.L. Pena, A. Dejoz, V. Fornes, F. Rey, M.I. Vazquez, J.M. Lopez Nieto, *Appl. Catal. A* 209 (2001) 155.
- [9] H. Berndt, A. Martin, A. Bruckner, E. Schrier, D. Muller, H. Kosslick, G.V. Wolf, B. Lucke, *J. Catal.* 191 (2000) 284.
- [10] S. Shylesh, A.P. Singh, *J. Catal.* 228 (2004) 333.
- [11] P.T. Tanev, M. Chibwe, T.J. Pinnavaia, *Nature* 368 (1994) 321.
- [12] S. Gontier, A. Tuel, *Stud. Surf. Sci. Catal.* 97 (1995) 157.
- [13] N. Ulagappan, C.N.R. Rao, *J. Chem. Soc. Chem. Commun.* (1996) 1047.
- [14] W.A. Carvalho, P.B. Varaldo, M. Wallau, U. Schuchardt, *Zeolites* 18 (1997) 408.
- [15] K. Chaudhari, T.K. Das, P.R. Rajmohan, K. Lazar, S. Sivasanker, A.J. Chandwadkar, *J. Catal.* 183 (1999) 281.
- [16] T.K. Das, K. Chaudhari, A.J. Chandwadkar, S. Sivasanker, *J. Chem. Soc. Chem. Commun.* (1995) 2495.
- [17] A. Corma, M.T. Navarro, M. Renz, *J. Catal.* 219 (2003) 242.
- [18] A. Corma, H. Garcia, *Chem. Rev.* 103 (2003) 4307.
- [19] A.L. Wilds, *Org. React.* 2 (1994) 178.
- [20] Y. Ishii, T. Nakano, A. Inada, Y. Kishigami, K. Sakurai, M. Ogawa, *J. Org. Chem.* 51 (1986) 240.
- [21] B. Knaver, K. Krohn, *Liebigs Ann.* (1995) 677.
- [22] J.L. Namy, J. Soupe, J. Collin, H.B. Kagan, *J. Org. Chem.* 49 (1984) 2045.
- [23] J. Kaspar, A. Trovarelli, M. Lenarda, M. Graziani, *Tetrahedron Lett.* 30 (1989) 2705.
- [24] Y. Zhu, S. Liu, S. Jaenicke, G. Chuah, *Catal. Today* 97 (2004) 249.
- [25] S.H. Liu, S. Jaenicke, G.K. Chuah, *J. Catal.* 206 (2002) 321.
- [26] V.A. Inavov, J. Bachelier, F. Audry, J.C. Lavalley, *J. Mol. Catal.* 91 (1994) 45.
- [27] M.A. Aramendia, V. Borau, C. Jimenez, M. Marinas, J.R. Ruiz, F.J. Urbano, *J. Colloid Interf. Sci.* 238 (2001) 385.
- [28] J.C. van der Wall, P.J. Kunkeler, K. Tan, H. van Bekkum, *J. Catal.* 173 (1998) 74.
- [29] Y. Zhu, G. Chuah, S. Jaenicke, *J. Catal.* 227 (2004) 1.
- [30] A. Corma, M.E. Domine, S. Valencia, *J. Catal.* 215 (2003) 294.
- [31] P.J. Kunkeler, B.J. Zuurdeeg, J.C. van der Waal, J.A. van Bokhoven, D.C. Koningsberger, H. van Bekkum, *J. Catal.* 180 (1998) 234.
- [32] E.J. Croyghton, S.D. Ganeshie, R.S. Downing, H. van Bekkum, *J. Mol. Catal. A* 115 (1997) 457.
- [33] J.C. van der Waal, E.J. Croyghton, P.J. Kunkeler, H. van Bekkum, *Top. Catal.* 4 (1997) 261.
- [34] T.M. Jyothi, T. Raja, K. Sreekumar, M.B. Talawar, B.S. Rao, *J. Mol. Catal. A* 157 (2000) 193.
- [35] R. Anwender, C. Palm, G. Gerstberger, O. Groeger, G. Engelhardt, *Chem. Commun.* (1998) 1811.
- [36] D. Zhao, Q. Huo, J. Feng, B.F. Chmelka, G.D. Stucky, *J. Am. Chem. Soc.* 120 (1998) 6024.
- [37] T. Chirayil, P.T. Zavalij, M.S. Whittingham, *Chem. Mater.* 10 (1998) 2629.
- [38] J. George, S. Shylesh, A.P. Singh, *Appl. Catal. A: Gen.* 290 (2005) 148.
- [39] S. Shylesh, A.P. Singh, *J. Catal.* 233 (2005) 359.
- [40] S.R.J. Davis, Z. Liu, *Chem. Mater.* 9 (1997) 2311.
- [41] K. Kosuge, D.S. Singh, *J. Phys. Chem. B* 103 (1999) 3563.
- [42] X. Wang, H. Xu, X. Fu, P. Liu, F. Lefebvre, J.M. Basset, *J. Mol. Catal. A: Chem.* 238 (2005) 185.