Synthesis, characterization and catalytic performance of Sn-MCM-48 in solvent-free Mukaiyama-type aldol condensation reactions

U.S. Taralkar [1], P. Kalita, R. Kumar [2], P.N. Joshi *

Catalysis Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, India

ABSTRACT

The influence of various synthesis variables on the physico-chemical properties of mesoporous stannosilicate molecular sieves with MCM-48 structure (Sn-MCM-48) has been investigated. Sn-MCM-48 has been used as a new heterogeneous catalyst in solvent-free Mukaiyama-type aldol reactions. Invariably, the β-hydroxy ester selectivity was found to be 100% irrespective of the conversion level. The product yield was found to increase, to reach a maximum (70%), and then to decrease with the increase in tin content.

1. Introduction

The discovery of the M41S family of mesoporous silicas [1–4] brought about the beginning of a new age for open-structured inorganic materials by expanding the range of uniform pore sizes from microporous into the mesopore range. Among the members of this novel M41S family, cubic MCM-48 phase exhibits a structure consisting of an enantiomeric pair of separate three-dimensional channel systems [5]. By virtue of its structural characteristics, MCM-48 has demonstrated its potential use as a promising catalyst/catalyst support, adsorbent, sensor and an excellent inorganic template for the synthesis of nanostructures [6–11]. However, MCM-48 has been studied less often than MCM-41, which can be attributed in part to the fact that its synthesis requires more specific conditions. Since Si-MCM-48 possesses a neutral framework, it has been used as a catalyst support rather than as a catalyst. In view of making the materials more active for various suitable catalytic applications, fewer investigations were devoted to synthesis, characterization and catalytic applications of MCM-48 with framework-substituted, -grafted or -immobilized metal heteroatoms or

their complexes [6,12–19]. Lewis acids have proved their potential in a variety of organic transformation reactions of commercial importance [20]. As a consequence of the inherent advantages of heterogeneous processes, much effort has been directed towards development of solid Lewis acids. Generation of stronger Lewis acid sites by substituting Sn in the silica framework can be rationalized by the higher atomic size and electronegativity. Interesting results regarding oxidation over Sn-substituted MCM-41 and MSU-type mesoporous silica have also been reported [21–23]. Moreover, enhanced structural stability has been shown [24] by Sn-infused MCM-41. The activity of Sn-ZSM-5 in carbon–carbon bond formation reactions was found to be higher than Al-ZSM-5 and its ion-exchanged analogues [25]. It is, however, noteworthy here that despite the significance of Sn-incorporated catalysts, the synthesis, characterization and catalytic application of mesoporous stannosilicate molecular sieves with MCM-48 structure (Sn-MCM-48) have not been systematically explored.

In the current work, we describe the systematic studies on the hydrothermal synthesis of Sn-MCM-48 from gels containing relatively lower amounts of surfactant and water. The procedure employed has allowed us to obtain the products from relatively low volumes of synthesis gel and in shorter synthesis periods at 408 K. Furthermore, since cetyltrimethyl ammonium hydroxide (CTAOH) serves as a simultaneous source of surfactant and OH⁻ species, only source materials, CTAOH solution and water are required to prepare the starting synthesis gel. Attempts were also made to establish the cause-and-effect relationships among

synthesis variables such as synthesis time, molar SiO_2/SnO_2 ratios in the starting gel composition, silica sources and tin sources, and the physico-chemical properties of Sn-MCM-48 materials. The well-characterized Sn-MCM-48 materials have been used, for the first time, as a new heterogeneous catalyst in Mukaiyama-type aldol reaction, a facile method for the formation of carbon–carbon bond under solvent-free system, since this reaction is known to be a Lewis acid-catalyzed reaction.

2. Experimental

2.1. Materials

The hydrothermal syntheses of Si-MCM-48 and Sn-MCM-48 were carried out using 25 wt.% cetyltrimethyl ammonium hydroxide (CTAOH) solution in methanol (Dishman Pharmaceutical and Chem. Ltd., Mumbai, India) and distilled water. Two different silica sources viz. (i) fumed silica (99%, Aldrich), (ii) silica sol (99%, 40 wt.% SiO_2, V.P. Chemicals, Pune, India) and two different tin sources viz. (i) tin tetrachloride pentahydrate (98%, Loba Chemie, India) and (ii) sodium stannate (95%, Aldrich) were used in the present work.

2.2. Hydrothermal synthesis

The hydrothermal synthesis of Sn-MCM-48 was carried out using gels comprising molar ratios of $CTAOH/SiO_2 = 0.33$, $H_2O/SiO_2 = 25$ and $SiO_2/SnO_2 = 50$–250 at 408 K in static conditions under autogeneous pressure. The details of each system showing the individual gel composition and the sources used are presented in Table 1. Each system was subjected to the identical set of synthesis conditions including down-stream processing to investigate the influence of the target parameter on the quality of the phase formed. In a typical synthesis of Sn-MCM-48 (system V in Table 1), 0.143 g of $SnCl_4·5H_2O$ dissolved in 45 g of water was slowly added to 39.73 g of CTAOH solution with constant stirring. The reaction mixture was further stirred for 15 min and then 6 g of fumed silica was added slowly under constant stirring. After continuous stirring for 2 more hours at room temperature, the resultant gel was transferred into a Teflon-lined stainless steel autoclave. After being sealed, it was heated at 408 K for desired length of period. The time at which the autoclave attained the 408 K temperature was taken as a reference to determine the length of period. After the autoclave was cooled to room temperature, the product was recovered by filtration, washed repeatedly with distilled water and then dried at 373 K for 4 h. Finally, the selected sample was subjected for the removal of the template by calcination in air at 813 K for 6 h.

In similar fashion, each system was prepared and subjected to hydrothermal conditions aiming at investigating the influence of each target synthesis parameter on the quality of the Sn-MCM-48

formed and finally on its catalytic performance. For comparison purposes, Si-MCM-48 was also prepared (system VIII in Table 1) by heating a gel having the same molar composition but with no tin tetrachloride at 408 K, using fumed silica as source of silica.

2.3. Characterization

Powder X-ray diffractograms of as-prepared and calcined samples were recorded on a Rigaku Miniflex (Japan) diffractometer using Cu–Kα radiation. The diffraction data were recorded in the 2θ range of 1.5–10° with a scanning rate of 1° min^{-1}. 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 the BET method. The pore size distribution was calculated using desorption branches of nitrogen isotherms and the BJH method. The TEM images were scanned on a JEOL JEM-1200EX instrument with 100 kV of acceleration voltage. The diffuse reflectance UV–vis spectra were recorded in the range 200–800 nm with a Shimadzu UV-2101 PC spectrometer. The chemical compositions of the samples were established by atomic absorption spectrometry (Varian SpectrAA 220 FS).

2.4. Catalytic testing

Catalytic liquid-phase Mukaiyama–aldol condensation reaction of methyl trimethyl silyl dimethylketene acetal and benzaldehyde was performed under solvent-free system. The reaction was carried out in a two-necked round-bottom flask equipped with a water condenser during vigorous stirring in N_2 atmosphere. The catalyst was preactivated at 523 K before the reaction in a vacuum oven and subsequently used for the reaction under extremely dry conditions. In a typical procedure, 10 mmol of 1-methoxy-2-methyl-1- (trimethylsiloxy) propene, 10 mmol of benzaldehyde and 0.348 g of pre-activated catalyst were stirred in a 25 ml round-bottom glass flask for 24 h at 373 K under nitrogen atmosphere. Analyzing the products at the end of 0.5, 1, 1.5, 2, 3, 6, 12 and 24 h monitored the progress of the reaction. The catalyst was separated by centrifugation/filtration and then the filtrate was washed twice with 1N HCl and then diluted with water and extracted with DCM (3×15 ml). The organic layer was separated and dried with anhydrous Na_2SO_4. The solvent was removed using a rotary evaporator (Rotavapor R-114, BUCHI) to produce the crude product. The product was further purified through column chromatography using silica gel (100–200 mesh), (petroleum ether: ethyl acetate = 3:1) and confirmed through GC, GC–MS, ^{1}H NMR, and ^{13}C NMR measurements.

3. Results and discussion

3.1. Structural development

Since, the synthesis time is a critical variable in the formation of M41S materials [26], time-dependent studies for the monitoring of the degree of ordering of the pore structures (structural regularity) of MCM-48 have been conducted for each system that is described in Table 1. The results obtained from system V are presented here as an illustrative example. The XRD profiles showing structural development of Sn-MCM-48 during progressive hydrothermal synthesis are depicted in Fig. 1. As time progresses, the intensity of the characteristic peaks increases, reaches a maximum and then decreases on further heating. Similarly, shifting of characteristic peaks towards lower 2θ occurs with time, reaches a minimum and then starts shifting to higher 2θ value on further heating. Simultaneous increase in peak intensity and shifting of the peak to lower 2θ values suggest that the growth of the unit cell occurs

Table 1
Details of different systems, their molar gel compositions and type of source materials used for hydrothermal synthesis at 408 K, under autogeneous pressure and at static conditions.

System designation	Molar gel composition				Sources	
	SiO_2	CTAOH	H_2O	SnO_2	Silica	Tin
I	1	0.33	25	0.02	Fumed silica	$SnCl_4·5H_2O$
II	1	0.33	25	0.01	Fumed silica	$SnCl_4·5H_2O$
III	1	0.33	25	0.0067	Fumed silica	$SnCl_4·5H_2O$
IV	1	0.33	25	0.005	Fumed silica	$SnCl_4·5H_2O$
V	1	0.33	25	0.004	Fumed silica	$SnCl_4·5H_2O$
VI	1	0.33	25	0.004	Fumed silica	Sodium stannate
VII	1	0.33	25	0.004	Silica sol	$SnCl_4·5H_2O$
VIII	1	0.33	25	–	Fumed silica	–