PREPARATION AND CHARACTERISATION OF PURE AND HYBRID MCM-41 & MCM-48

A

Thesis Submitted

In partial fulfillment for the award of the degree for

MASTER OF SCIENCE

IN

CHEMISTRY

Submitted By:

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THAPAR UNIVERSITY

JULY, 2011

Dedicated

to

My Parents

CANDIDATE'S DECLARATION

I hereby declare that the work being presented in the thesis entitled, **"Preparation and characterisation of pure and hybrid MCM-41 & MCM-48"**, in partial fulfillment of the requirement for the award of the degree of **Masters of Science in Chemistry in the School of Chemistry and Biochemistry, Thapar University, Patiala,** is my own work during the period of January 2011 to July 2011, under the supervision of **Dr. Amjad Ali,** Assistant Professor, School of Chemistry and Biochemistry, Thapar University, Patiala. I have not submitted the matter embodied in this thesis for the award of any other degree.

Rinipal Kaur
Rinipal Kaur

Patiala

Date: 15th July, 11

This is to certify that the above statement made by the candidate is correct and true to the best of our knowledge.

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CERTIFICATE

This is to certify that the thesis entitled **"Preparation and characterisation of pure and hybrid MCM-41 & MCM-48"**, being submitted by Rinipal Kaur to **Thapar University, Patiala**, in partial fulfillment of the requirement for the award of the degree of Master of Science in Chemistry, is a bonafide work carried out under my supervision, and that no part of this thesis has been submitted for the award of any other degree.

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Life at Thapar University could not be imagined without golden friends like Adeti, Jaspreet, Nayanjot and Shilpa, with whom I have shared the best time of my life and who were always there in the hour of need.

Place: Patiala
Date: 15th July, 11

Regards,
Kinipal Kaur
(KINIPAL KAUR)

LIST OF CONTENT

ABSTRACT

In the present thesis the synthesis and characterization of SiO_2, Al/SiO_2 and Ti/SiO_2 is described. MCM-41 (Mobil composition of matter No.41) exhibiting hexagonal arrangement of mesopores in the range of 15-100Å had been synthesized using cetyltrimethylammoniumbromide (CTAB) as surfactant and tetraethylorthosilicate (TEOS) as silica source. Other members of this family exhibiting cubic symmetry, had also been synthesized namely MCM-48 (Mobil composition of matter No.48) using cetyltrimethylammoniumbromide (CTAB) as surfactant and tetraethylorthosilicate (TEOS) as silica source and ethanol as cosolvent. Aluminium was further incorporated to get hybrid MCM-41 mesoporous structures using aluminium isopropoxide as aluminium source, cetyltrimethylammoniumbromide (CTAB) as precursor agent and tetraethylorthosilicate (TEOS) as silica source. The acidic strength of the prepared catalyst was determined by Hammett indicator tests. Further, sol-gel technique for the preparation of Ti/SiO_2 material was employed using titanium isopropoxide as titanium source, silica gel as silica support and isopropanol as cosolvent. The prepared samples had been characterized by powder X-ray diffraction (XRD), Fourier transformed infrared (FT-IR) techniques and scanning electron microscopy (SEM).

CHAPTER 1

INTRODUCTION AND LITERATURE SURVEY

1.1 INTRODUCTION

With the advances in catalysis, adsorption, guest-host chemistry, drug delivery systems, biosensors, nanodevices, bio-immobilization, ion exchange, optics and photovoltaic which require the development of ordered porous materials with controllable structures and systematic pore architecture urged into the synthesis of mesoporous materials. Till 1990, heterogeneous catalysis over zeolites was restricted to the materials with pore sizes less than 20 Å. Therefore, pore enlargement was one of the main aspects in zeolite chemistry. Now the effort has been devoted to develop frameworks within the mesoporous range. The discovery of mesoporous molecular sieves, MCM-41 & MCM-48 (Mobil composition of matter No.41 & No.48 respectively) possesses a regular array of uniform pore openings is seeking much attention.[1] It has opened a new idea for creating zeotype materials.[2] The key to form such adsorbents is to use organic templates, which form organic–inorganic mesophases. The two most investigated materials, MCM-41 with a 2-D hexagonal structure and MCM-48 with a 3-D cubic structure, are synthesized using n-alkylammonium salts as templates.[3,4] A range of templates have are employed for the synthesis of ordered mesoporous silica, such as non-ionic, polar, low molecular weight compounds, e.g. n-alkylamines[5] and polymers and co-polymers and tetraethylorthosilicate (TEOS) as silica source. Further mesoporous structure can be controlled by adding auxiliary organic chemicals (e.g., mesitylene) and changing reaction parameters (e.g., temperature, compositions).[2] Mesoporosity can also endow a material with a high surface area exceeding 1,000m^2/g and pore volume greater than 1cm^3/g. This greatly expands the potential of the materials for application to adsorption and as a support for immobilized catalytic or sensing moieties.[6]

In present work MCM-41, MCM-48 has been synthesized. Further aluminium was incorporated to get aluminosilica mesoporous materials with different ratios of Al/TEOS and their acidic strengths were measured by Hammett indicators. Then the sol-gel synthesis of TiO_2-SiO_2 has been performed which has large surface area and good sedimentation ability. The prepared sample has been characterized by powder X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM).

1.2 LITERATURE SURVEY

Porous molecular sieves are extensively used as adsorbents, catalysts and catalyst supports as they have high surface areas. According to IUPAC definition[7] porous materials are divided into three types based on their pore dimensions shown below in Table.1.

Table 1: Type and pore size of porous materials

TYPE	*PORE SIZE(Å)*
Microporous	<20
Mesoporous	20-500
Macroporous	>500

Well-known members of the microporous materials are Zeolites[8] and aluminophosphate molecular sieves.[9] Zeolites are hydrated, crystalline, microporous aluminosilicates, constructed from TO_4 tetrahedra (T = tetrahedral atom, e.g., Si, Al) connected by oxygen atoms. These materials possess uniform channels associated by rings of a definite number of T atoms. The characteristics of their structure are thermal stability, different acid sites and acidity, ion exchange properties, shape and size-selective pores and channels of zeolites which have been well established. Now days modified framework and incorporation of different species make these materials catalytically active. Earlier heterogeneous catalysis over zeolites was limited to the materials with pore sizes less than 20Å. Therefore, pore enlargement was one of the main aspects in zeolite chemistry. Considerable synthetic effort has been given to develop frameworks within the mesoporous range. In 1992, scientists in Mobil Oil Corporation research group discovered the new family of mesoporous siliceous materials designated as M41S with exceptionally large and uniform pores.[3,4] These materials possess well-defined pores, whose diameters are in the range of 15-100Å. At the beginning, three members of the

M41S family of materials were introduced, namely MCM-41, MCM-48 and MCM-50. The pores of MCM-41 were considered to be obtained from silicate condensation about separate cylindrical micelles, whereas the ordering of structure results from the hexagonal arrangement of the silica-encased micellar array. The material has one dimensional channel system,[3,4] resembling a honeycomb network. The structure of MCM-48 is more complex than the straightforward case of the hexagonal one-dimensional MCM-41. It is analogous to that of liquid crystal like material with the cubic Ia3d symmetry. There are several proposals about the mechanism of formation of the cubic liquid crystal phase such as independent, mutually intertwined arrangements of surfactant rods towards a complex, periodic minimal energy surface structure.[10,11] The structure has cubic symmetry and contains two intersecting unique three-dimensional channel system. The structure of the stabilized lamellar MCM-50 belongs to the same proposed structure of a lamellar liquid crystal phase. The classification of the family of mesoporous materials according to their different symmetry is given in Table 2 and Fig 1.

TABLE 2: The classification of mesoporous materials[12]

Crystal system	***Example***	***Pore system***	***Space group***
Hexagonal	MCM-41	1-D	p6mm
Cubic	MCM-48	3-D	Ia3d
Stabilized lamellar	MCM-50	2-D	
Cubic	SBA-1		Pm3n
Hexagonal	SBA-3	2-D	P6mm

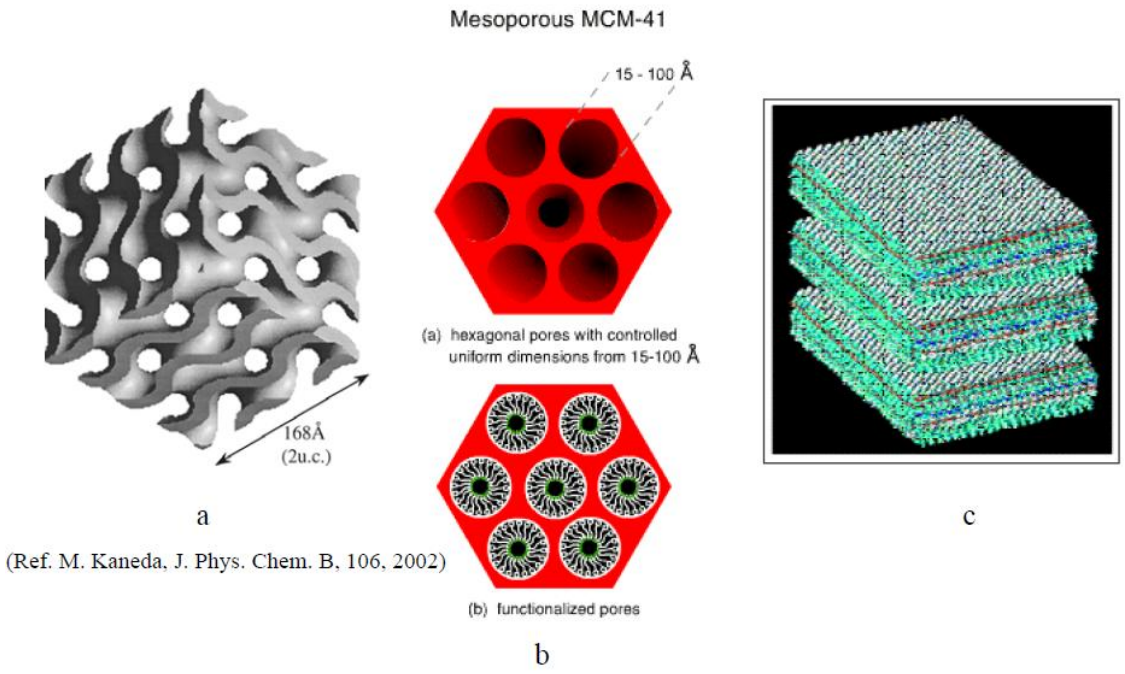


Figure 1: (a) Model of the three dimensional structure of cubic MCM-48 (b) one dimensional hexagonal MCM-41 (c) stabilized structure of MCM-50

The synthesis procedures of MCM-48 and MCM-41 are almost identical and MCM-48 is as reproducible as MCM-41[3]. Similarities between MCM-48 and MCM-41 are as follows[25]: MCM-48 can be as easily synthesized as MCM-41 and the porosity of MCM-48 is similar to that of MCM-41. MCM-48 and MCM-41 have similar chemical and thermal stability. But the difference lies in the fact that three dimensional channel systems in MCM-48 is much more desirable than a one-dimensional MCM-41 in catalytic point of view. Narrow pore size distribution and its regular cubic pore structure makes MCM-48 as a matrix to immobilize catalytically active species.[10,14] Therefore, it is necessary to find a flexible and fast synthesis route that allows control over shape and porosity of MCM-48. The present work has been devoted to develop a reliable synthesis route for the preparation of highly crystalline and reproducible MCM-48.

APPLICATIONS OF M41S MATERIALS

Defect free siliceous mesoporous molecular sieve with composition of SiO_2 are electrically neutral and this leads to a lack of strong intrinsic surface acidity. Various attempts were made to incorporate transition metal atoms as well as main group elements into mesoporous silica. Substitution of trivalent cations such as B^{+3}, Ga^{+3}, Al^{+3} and Fe^{+3} [13] for silicon in the wall of the mesoporous silica, results a negative framework charge, which can be compensated by protons providing catalytically active acid sites. The number of acid sites and strength is related to the amount and nature of the incorporated metal. These materials are used in acid catalyzed reaction and the main applications are in petroleum refining processes.[13,14]

The Ti, V and Cr containing MCM-41 & MCM-48 molecular sieves are active catalysts for oxidative double bond cleavage of methyl methacrylate pyruvate and benzaldehyde as the dominant respective products.[15] TiO_2-SiO_2 supported catalyst act as photocatalyst for β-napthol photo degradation.[16] Zr MCM-41 has been found to be active toward the dehydration of isopropyl alcohol.[17] A few reports describe the synthesis and characterization of mesoporous silica modified by metals like Mn or Mo[18] which have been found to be catalytically active in the hydroxylation of phenol, 1-napthol and oxidation of aniline with aqueous H_2O_2. It has been reported that Co and Mo incorporated Al-MCM-41 shows higher hydrogenation and hydrocraking activities than Co-Mo/Al_2O_3 catalysts.

Chemistry of Surfactant/Silicate Aqueous Solution

Knowledge of the chemistry of surfactant/silicate solution is a required for understanding the synthesis and mechanisms responsible for the formation of MCM-41 from its precursors.

Behavior of Surfactant Molecules in an Aqueous Solution.

In a simple binary system of water-surfactant, surfactant molecules arrange themselves as very active components with different structures in accordance with increasing concentrations, as schematically shown in Figure 2. At low concentrations, they energetically exist as monomolecules. With increasing concentration surfactant molecules aggregate together to form micelles in order to decrease the system entropy. The initial concentration threshold at which monomolecules aggregate to form isotropic micelles is called cmc (critical micellization concentration).

As the concentration process continues, hexagonal close packed arrays appear, producing the hexagonal phases. The next step in the process is the collapsing of the adjacent, mutually parallel cylinders to produce the lamellar phase. In some cases, the cubic phase also appears prior to the lamellar phase. The cubic phase is generally believed to consist of complex, interwoven networks of rod-shaped aggregates.

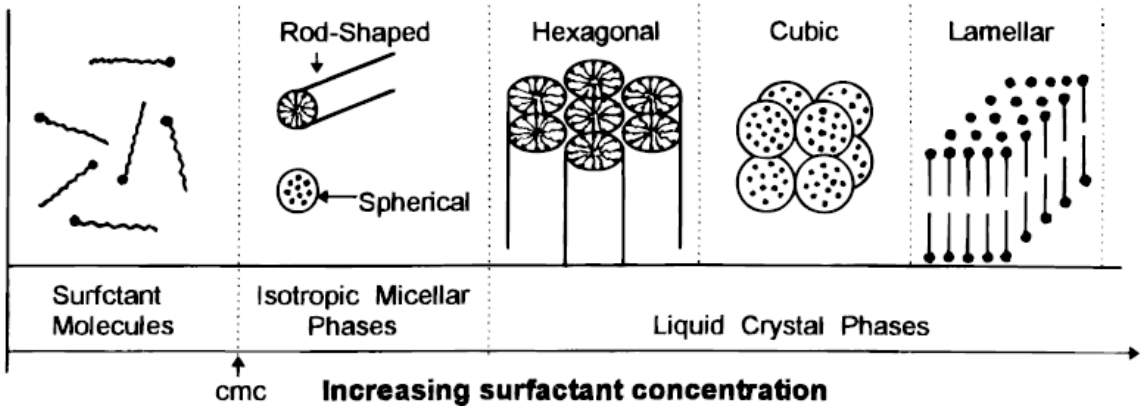


Figure 2: Phase sequence of surfactant-water binary system[19]

Synthesis mechanism of M41S materials

The most important feature of the preparation of the M41S materials is the role of the templating agents during the synthesis. The template molecules used are not single solvated organic cations as used in zeolite synthesis, but the surfactants built molecular arrays, which form complex micelles around which the main meso structure is built up. Surfactants are large organic molecules having a long hydrophobic tail of variable length (e.g. alkyltrimethylammonium cations with the general formula $C_nH_{2n+1}(CH_3)_3\ N^+$, where

n > 8) and a hydrophilic head. The schematic diagram of the formation of microporous and mesoporous material is given in Fig 3. Similar to zeolite synthesis where organic molecules play an essential role as structure directing agents (SDA), surfactants act as templates forming an ordered organic inorganic composite material.[20] The idea of formation of the organic-inorganic composites is based on the electrostatic interactions between the positively charged surfactants and the negatively charged silicate species. During the synthesis mechanism surfactants aggregate with their hydrophobic tails exposing their polar heads to the aqueous solution to form complex micelles. When silica is introduced, there is a charge balance between the surfactant and silicate ion pairs in which the silicate material formed inorganic walls between ordered surfactant micelles.

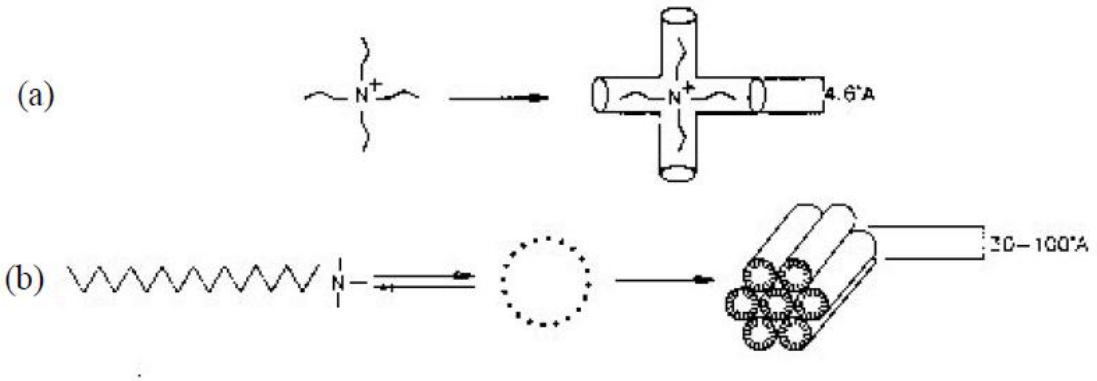


Figure 3: The schematic diagram for the formation of (a) microporous material using individual short alkyl chain quaternary ammonium compound (b) mesoporous materials using long chain alkyl quaternary ammonium compound[1]

According to the liquid crystal templating (LCT) mechanism two different pathways[1,21] were described for the formation of the mesoporous systems with cetyltrimethylammoniumbromide (CTAB) used as SDA. The two pathways can be described as follows:

1. The liquid crystal phase is intact before the silicate species are added. First there is the formation of the hexagonal liquid-crystal phase around which the growth of the inorganic materials occurs. The surfactant micelles arrange together to form hexagonal arrays of rods. Silicate anions in the reaction mixture interact with the surfactant head group at the micelle water interface. Silica oligomers are formed by either acid or base catalyzed

hydrolysis of the silicate species, which then condense into a silica structure maintaining the structure of the liquid crystal precursor.

2. Addition of silicate resulting in the ordering of the silicate-encased surfactant micelles. To increase this effect, the randomly ordered rod like micelles react with the silicate species by columbic interactions to produce two or three monolayers of silicate at the external surfaces of the micelles. This species pack in such a manner to form a energetically favored hexagonal mesoporous arrangement followed by silicate condensation. Hydrothermal treatment leads to the inorganic wall to condense.

In both of the cases the resultant silicate/surfactant structure mimics structures known from liquid crystal phases. The most accepted mechanism for formation of mesophases can be summarized shown in Figure 4.

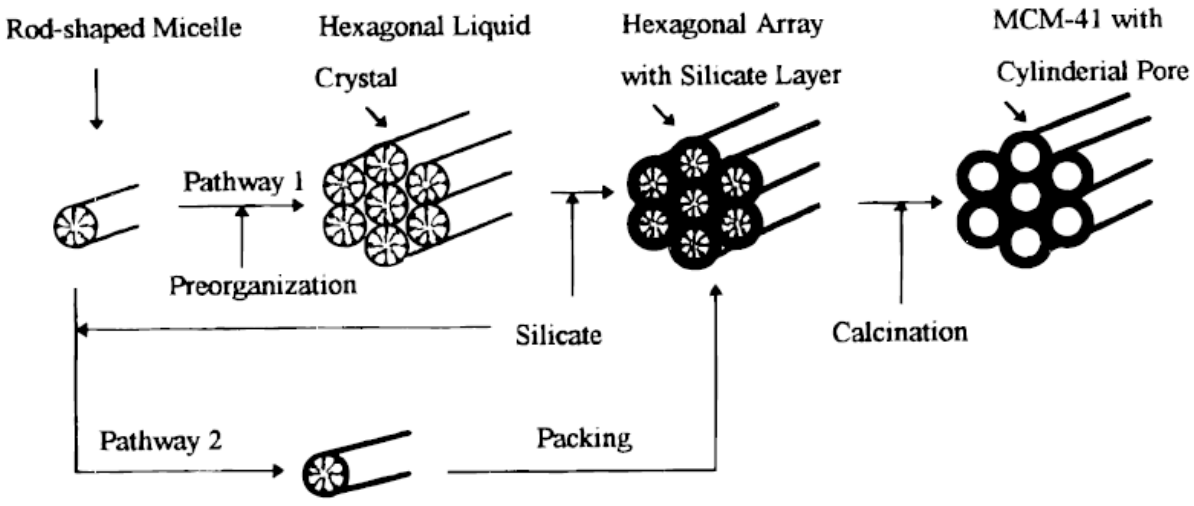


Figure 4: Schematic model of liquid crystal templating mechanism via two possible pathways[3]

CHAPTER 2

OBJECTIVES

OBJECTIVES

1. To synthesize MCM-41 and MCM-48 under the optimum synthesis conditions.
2. To incorporate aluminium in MCM-41 by varying aluminium to silica source ratios and to prepare Ti/SiO_2 materials by sol gel synthesis.
3. To characterize the prepared materials using powder XRD, FT-IR and SEM techniques.

CHAPTER 3

MATERIALS AND METHODS

MATERIALS AND METHODS

Surfactant Cetyltrimetylammonium bromide (CTAB), titanium isopropoxide as titanium source and silica gel were purchased from Sigma Aldrich. Tetraethylorthosilicate (TEOS), ethanol (99.9% pure), ammonia (33% pure), aluminum isopropoxide, sodium hydroxide, isopropanol (99.5% pure), methanol (99% pure) and HNO_3 (69-72% pure) were purchased from Loba chemie INDIA. Hammett indicators: neutral red, bromothmol blue, phenolphthalein, methyl orange and thymol blue were purchased from SD Fine Chemicals. All chemicals were used as received without further purification.

Powder X-ray diffraction (XRD) patterns were recorded on a Panalytical's X'Pert Pro with using monochromatic CuKα radiation (λ=1.54060 Å) in Thapar University, Patiala. Data were collected over a 2θ range of 2–10° for MCM-41, MCM-48 and Al/MCM-41 and 2θ=5-80° for TiO_2-SiO_2 material with a step size of 0.0260° at a scanning speed of 2°/min at an accelerating voltage of 45 kV and current of 40 mA. XRD was used to determine the particle size and the type of crystal planes found in the catalyst. Field emission scanning electron microscopy (FESEM) was performed on JEOL JSM 6510LV to collect the SEM images of the catalysts. The acidic strength of the Al/SiO_2 catalyst was determined by using the following Hammett indicators: neutral red (H_6.8), bromothymol blue (H_ = 7.2), phenolphthalein (H_ = 9.3), methyl orange (H_4.4) and thymol blue (H_2.8).

CHAPTER 4

PREPARATION AND CHARACTERISATION

4.1 PREPARATION

4.1.1 Preparation of MCM-41

MCM-41 was prepared by following the literature reported classical synthesis of MCM-41[22] with slight modification. In a typical preparation MCM-41 material was synthesized by dissolving 2.4 g of cetyltrimethylammonium bromide (CTAB) in 120 g of deionized water in a 250 ml round bottom flask and the reaction mixture was stirred at room temperature to obtain a clear homogenous solution. To this, 8 ml of ammonia (33% pure) was added and the mixture was stirred for 5 min followed by the addition of 10 ml of tetraethylorthosilicate (TEOS) to the same. The final molar composition of the gel was 1 M TEOS: 1.64 M NH_3: 0.15 M CTAB: 126 M H_2O. The reaction mixture was stirred for 12 h at room temperature and finally the mixture was filtered and washed consecutively with deionized water and ethanol. The semi-solid product thus obtained was calcinated at two different temp viz., 580°C and 680°C for 5 h.

4.1.2 Preparation of MCM-48

MCM-48 was prepared by following the literature reported synthesis of MCM-48 at room-temperature[23] with slight modification. Cetyltrimethylammonium bromide (CTAB) was dissolved in 50 g deionized water in a 250 ml round bottom flask and then 50 ml ethanol (99.9% pure) was added. Then 8 ml of ammonia (33% pure) was added and the mixture was stirred for 10 min at room temperature followed by the addition of 3.4 g of tetraethylorthosilicate (TEOS) to the same. The final molar composition of the gel was 1 M TEOS: 12.5 M NH_3: 54 M EtOH: 0.4 M CTAB: 174 M H_2O. The reaction was then stirred for 2 h and the solution was filtered, washed with deionized water and dried in air at room temperature. The solid product thus obtained was calcinated at 680°C for 6 h.

4.1.3 Preparation of hybrid Al/MCM-41

Al/MCM-41 was prepared by following the literature reported synthesis of aluminosilicate MCM-41[23] with slight modification. The aluminosilicate MCM-41 was prepared from a reaction mixture with the molar gel composition of: 1.00 M $Al(OiPr)_3$:

847 M H_2O: 4.33 NaOH: 0.95 M CTAB: 8.00 M SiO_2. Initially, 0.472 g of $Al(OiPr)_3$ was taken in a round bottom flask and 39.2 g of deionized water was added to it followed by the addition of 5 g of 2 M NaOH solution. The mixture was then stirred for 1 h to get clear solution of fully dissolved monomeric aluminum species in the solution. To this, 0.80 g of cetyltrimethylammonium bromide (CTAB) was added and the mixture was heated at 70°C to dissolve the surfactant. Finally, 3.85 g of tetraethylorthosilicate (TEOS) was added as the source of silica to the same and the resulted mixture was stirred at room temperature for 16 h. The product thus obtained was filtered and washed and calcinated at 500°C before sample characterization. The resulted Al/MCM-41 was expected to have 1.55 wt % aluminium.

In other experiments Al/MCM-41 was prepared in the same manner discussed above with the only difference that the amount of aluminium isopropoxide used was 0.1925 g and 0.5775 g to get different percentage of 0.62 % and 1.93 % aluminium respectively.

4.1.4Sol-gel synthesis of Ti/SiO_2

Preparation of Ti/SiO_2

Ti/SiO_2 material has been prepared by sol gel method and a typical procedure is as follows[26]:

In a 100 ml round bottom flask 20 ml of titanium isopropoxide (TIP) was added followed by the addition of 10 ml of isopropanol. The mixture was then stirred for 1 h to obtain a transparent TiO_2 solution. Then, the solution was diluted by adding 25 ml of distilled water and the pH of the solution was adjusted to 2 using 1M HNO_3, followed by stirring for 1 h to obtain a turbid TiO_2 colloid. 5 g silica gel was added to the TiO_2 colloid and the resulting mixture was stirred for 2 h at pH 3. The suspension so obtained was filtered and washed with deionized water to make the supernatant nearly neutral. The Ti/SiO_2 material so obtained was first dried at 70°C for 6 h and finally calcinated at 400°C for 2 h each.

4.2 CHARACTERISATION

4.2.1 CHARACTERISATION OF MCM-41

(A) X-ray Diffraction (XRD)

The XRD patterns of the prepare MCM-41 were recorded in the low angle range of 2θ~2-8° as shown in figure 5. The XRD pattern show the broad peaks, characteristic of mesoporous material. The XRD pattern of MCM-41 material prepared at 580°C calcinations temperature shows an intense peak at 2θ~2.5° and two less intense peaks at 4.4° and 5.3° corresponding to the d-values of 34.79, 19.92 and 18.34 Å respectively (fig 5A). These peaks have been indexed as (100), (110) and (200) reflections respectively. This type of diffraction pattern support the hexagonal structure[27,28] of MCM-41 with.[29]
The MCM-41 calcinated at 680°C show one intense peak (100) at 2θ~1.2° with d-spacing of 28.11Å but poor resolved peaks (110) and (200) (fig 5B) indicates imperfect 2-D hexagonal symmetry.

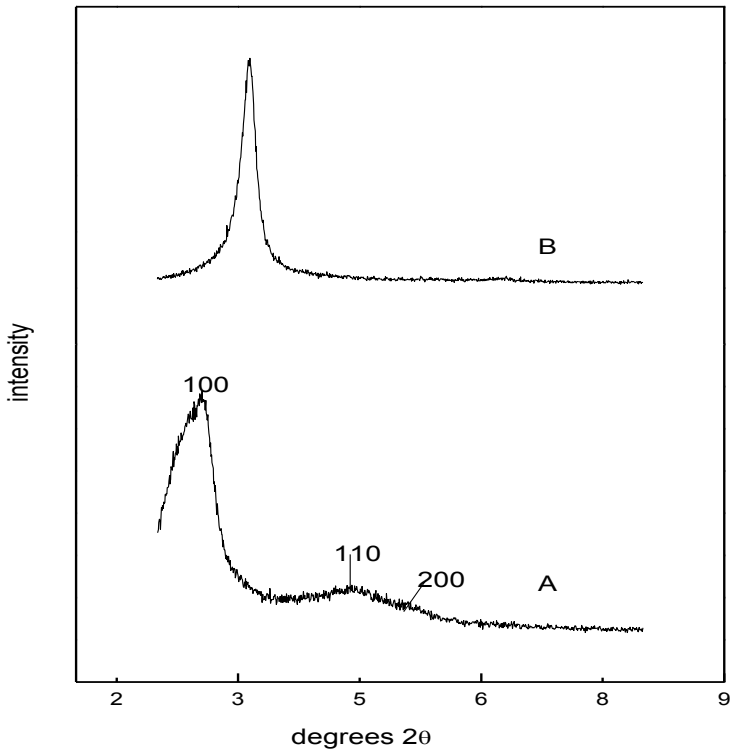


Figure 5: XRD of MCM-41 sample (A) calcinated at 580°C (B) calcinated at 680°C

(B) FT-IR spectra

The FT-IR spectra of prepared MCM-41 before calcination and post synthetic calcination are compared in Figure 6. The FT-IR spectrum of MCM-41 before calcination (fig 7A) shows characteristic peaks~1600 cm^{-1} due to the presence of -COOH group of organic template, while the peaks at 3500 cm^{-1} is due to -OH group and ~2900 cm^{-1} is due to the -CH vibrations of the template molecules. In the FT-IR spectra of the MCM-41 calcinated either at 580°C or 680°C (fig 6B and 6C), no peaks were observed due to surfactant supporting the removal of organic template after calcination. The peaks at 1096 cm^{-1} (Si-O-Si asymmetric vibration) and at 811 cm^{-1} (symmetric stretching of Si-O-Si) support the existence of Si-O-Si structure of MCM-41 material.[29]

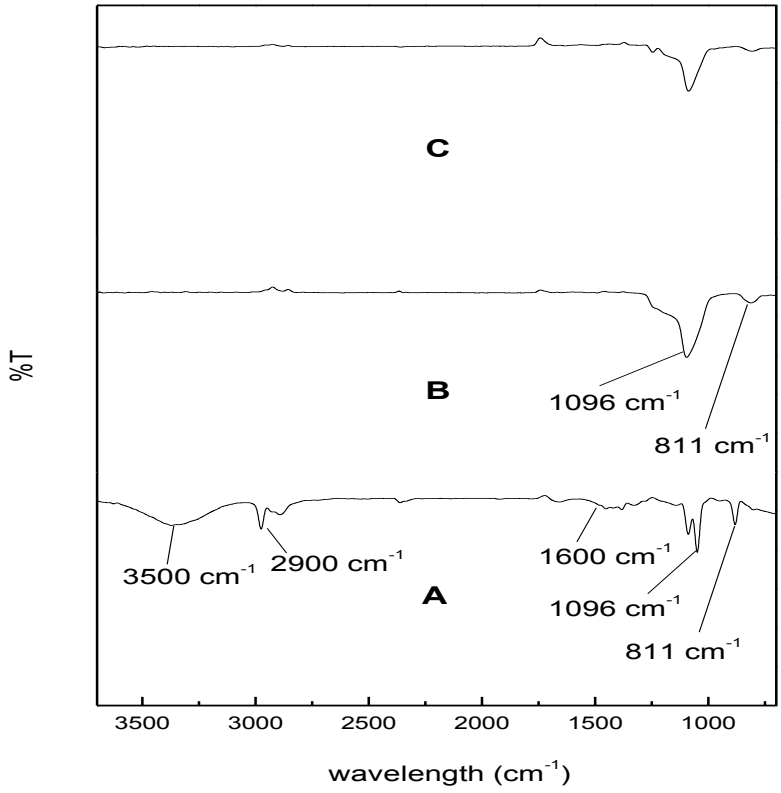


Figure 6: FT-IR of MCM-41 (A) before calcination (B) calcinated at 580°C (C) calcinated at 680°C

(C) SEM image

The surface morphology of the MCM-41 calcinated at 580°C, have been investigated by scanning electron microscopy as shown in Fig 7. The average size of the porous and irregular shaped catalyst particles by FESEM studies was found to be in the range of 0.5-2 μm.

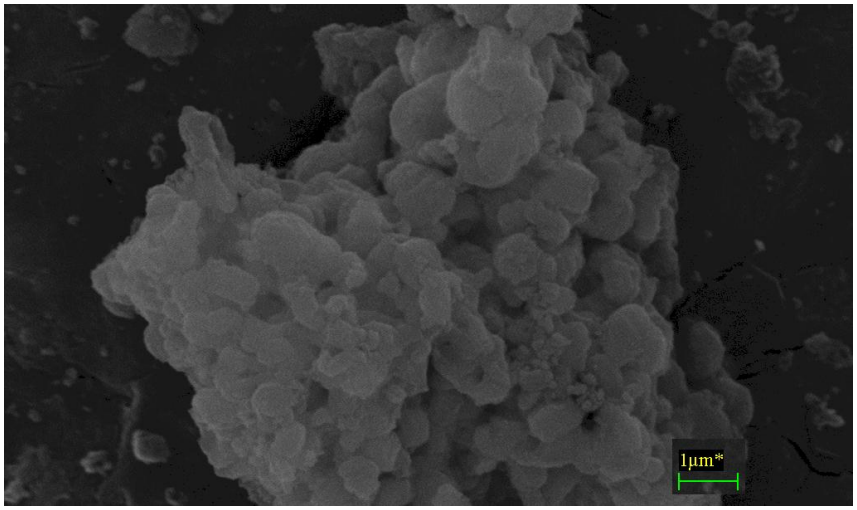


Figure 7: SEM image of MCM-41 calcinated at 580°C

4.2.2 CHARACTERIZATION OF MCM-48

(A) X-ray Diffraction (XRD)

The XRD patterns of the prepared MCM-48 were recorded in the low angle range of 2θ~0.5-10° as shown in Figure 8. The MCM-41 material prepared at 680°C calcinations temperature shows an intense peak at low angle of 2θ~0.5° and two less intense peaks at 1.2° and 2.05° corresponding to the d-values of 5801.44, 244 and 26.44 Å respectively. These peaks have been indexed as (211), (220), (321) reflection planes respectively (fig 8). This type of diffraction pattern support the cubic structure.[29]

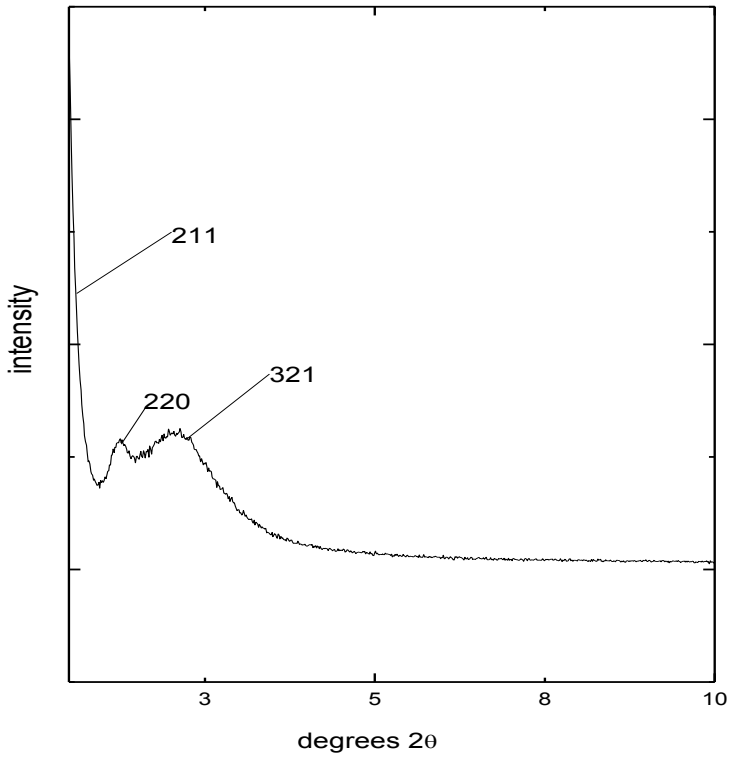


Figure 8: XRD of MCM-48 sample calcinated at 680^{0}C

(B) FT-IR spectra

The FT-IR spectra of prepared MCM-48 before calcination and post synthetic calcination are compared in Figure 9. The FT-IR spectrum of MCM-48 before calcination (fig 9A) shows characteristic peaks~1600 cm^{-1} due to the presence of -COOH group of organic template, while the peaks at 3400 cm^{-1} is due to -OH group and ~2900 cm^{-1} is due to the -CH vibrations of the template molecules. In the FT-IR spectra of the MCM-48 calcinated at 680°C (fig 6B), no peaks were observed due to surfactant supporting the removal of organic template after calcination. The peaks at 1095 cm^{-1} (Si-O-Si asymmetric vibration) and at 812 cm^{-1} (symmetric stretching of Si-O-Si) support the existence of Si-O-Si structure of MCM-48 material.[30]

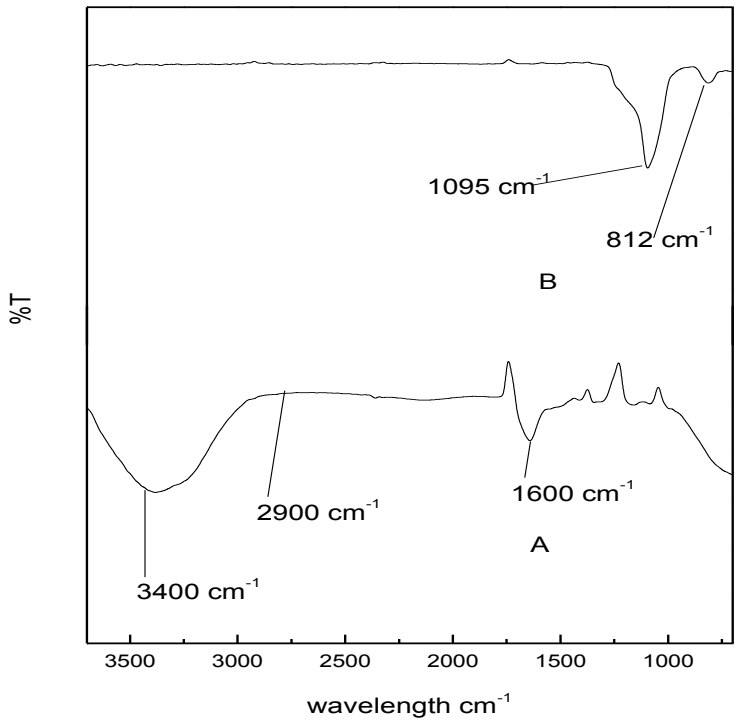


Figure 9: FT-IR of MCM-48 (A) before calcination (B) calcinated at 680°C

(C) SEM image

The surface morphology of the MCM-48 calcinated at 680°C, have been investigated by scanning electron microscopy as shown in Fig 10. The average size of the porous and spherical catalyst particles by FESEM studies was found to be in the range of 0.5-2 μm.

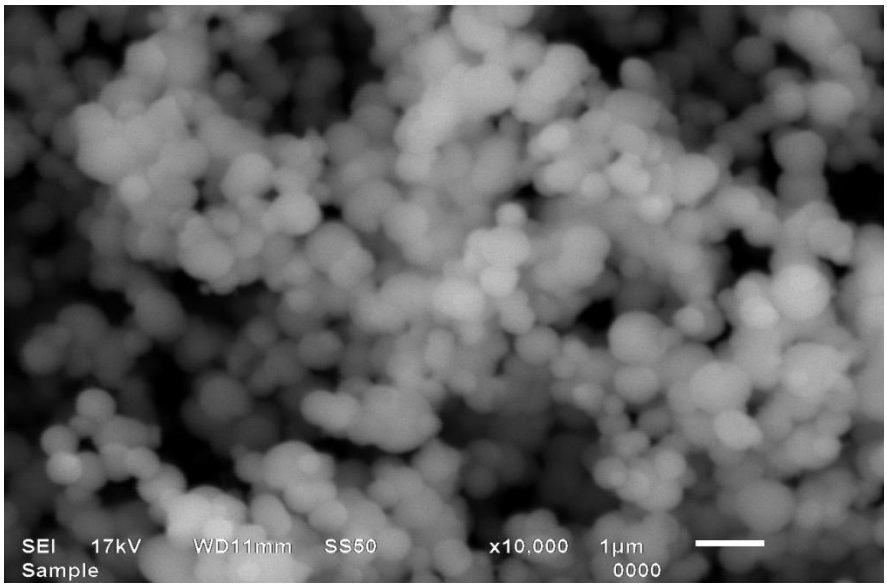


Figure 10: SEM image of MCM-48 calcinated at 680°C

4.2.3 CHARACTERIZATION OF Al/MCM-41

(A) X-ray Diffraction (XRD)

The XRD patterns of the prepared Al/MCM-41 were recorded in the range of 2θ~2-8° as shown in figure 11. The XRD patterns of Al/MCM-41 with varying wt % of aluminum i.e. 0.62 wt %, 1.55 wt % and 1.93 wt % are compared in (fig11 A, B and C) shows the broad peak, characteristic of mesoporous material.[24,25] Figure 11A clearly indicated strong intensity in XRD spectrum, suggesting that Al/MCM-41 with 1.93 wt % aluminium has higher order.

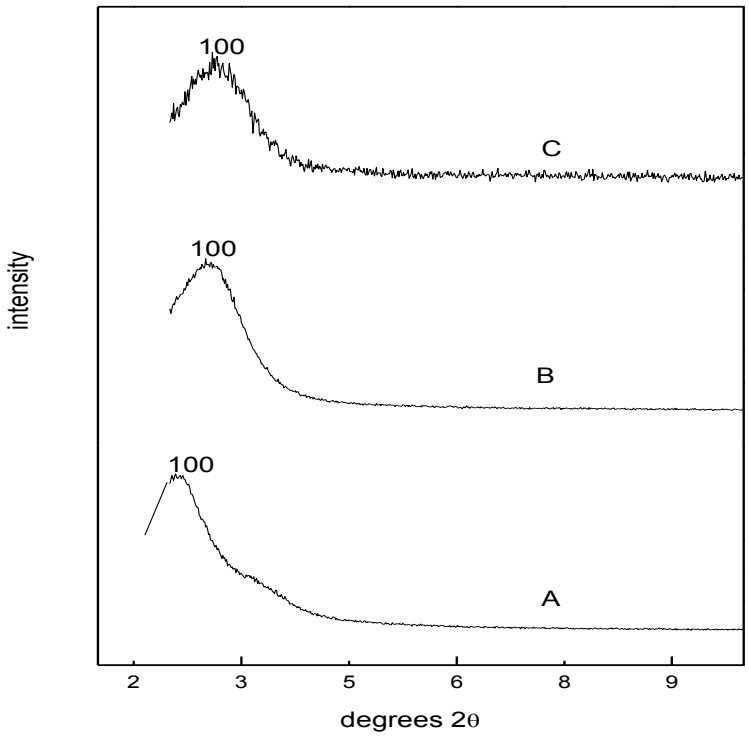


Figure 11: XRD of Al/MCM-41 (A) calcinated at 500°C with 0.62 wt % (B) calcinated at 500°C with 1.55 wt % (C) calcinated at 500°C with 1.93 wt %

(B) FT-IR spectra

The FT-IR spectra of prepared Al/MCM-41 with varying wt % of aluminium are shown in figure 12. In the FT-IR spectra of the Al/MCM-41 calcinated at 500°C with any wt % of no peaks were observed due to surfactant supporting the removal of organic template after calcination. The peaks at 1054 cm^{-1} (Si-O-Si asymmetric vibration) and at 796 cm^{-1} (symmetric stretching of Si-O-Si) support the existence of Si-O-Si structure of MCM-41 material.[29]

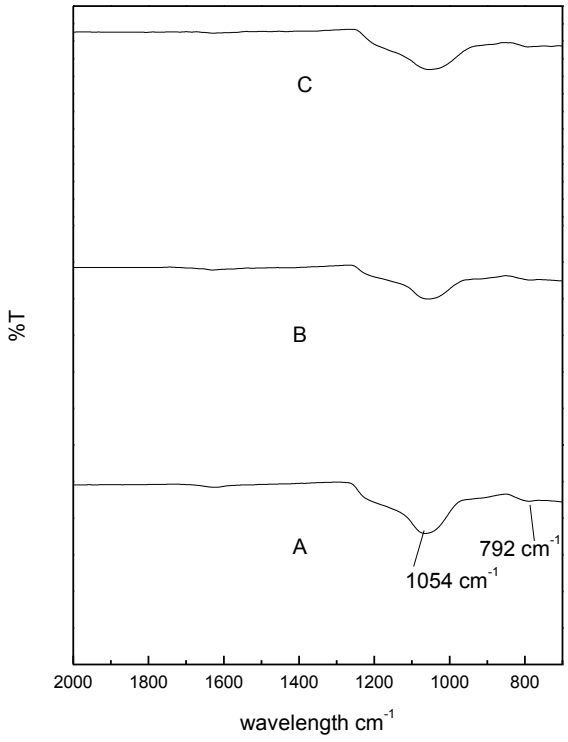
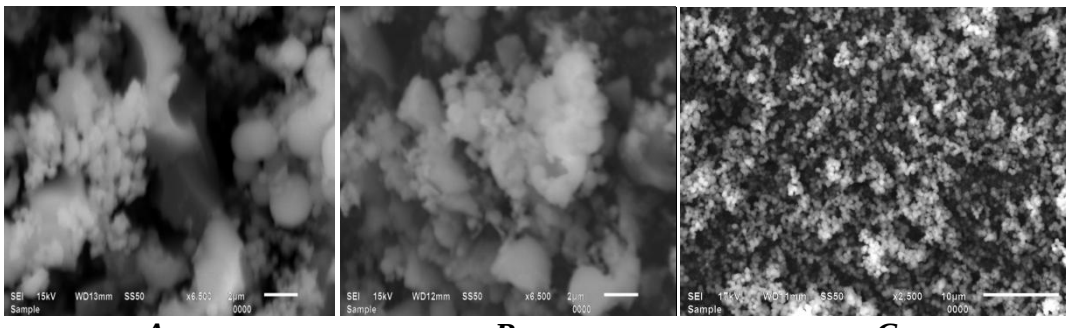


Figure 12: FT-IR of Al/MCM-41 (A) calcinated at 500°C with 0.62 wt % (B) calcinated at 500°C with 1.55 wt % (C) calcinated at 500°C with 1.93 wt %

(C) SEM image

The surface morphology of the Al/MCM-41 calcinated at 500°C, have been investigated by scanning electron microscopy as shown in Fig 13. The average size of the porous and round catalyst particles by FESEM studies was found to be in the range of 2-4 μm.



A ***B*** ***C***

Figure 13: SEM image of Al/MCM-41 (A) with 0.62 wt % (B) with 1.55 wt% (C) with 1.93 wt%

(D) Determination of acidic strength

The acidic strengths of the catalysts (H_) were determined by using Hammett indicators. Approximately 25 mg of the catalyst was added in 5 ml of a solution of Hammett indicators diluted with methanol and was left to equilibrate for 2 h. After the equilibration, the color of the catalyst was noted. The acidic strength is given in table 3.

Table 3: Acidic strength of Al/MCM-41 at different wt %

S.NO	CATALYST TYPE	ACIDIC STRENGTH
1.	Al/MCM-41 (.62 wt %)	3.1 <H_< 4.4
2.	Al/MCM-41 (1.55 wt %)	3.1 <H_< 4.4
3.	Al/MCM-41 (1.93 wt %)	3.1 <H_< 4.4

4.2.4 CHARACTERIZATION OF Ti/SiO_2

(A) X-ray Diffraction (XRD)

The XRD patterns of the prepared Ti/SiO_2 material were recorded in the wide angle range of 2θ~5-70° as shown in figure 14. The XRD pattern show the broad peaks, characteristic of nano Ti/SiO_2 mesoporous material. In the range from 2θ~5-45° there are the major peaks of the three crystalline polymorphs rutile, anatase and brookite, no additional diffraction patterns could been seen which corresponds to crystalline titania.[26]

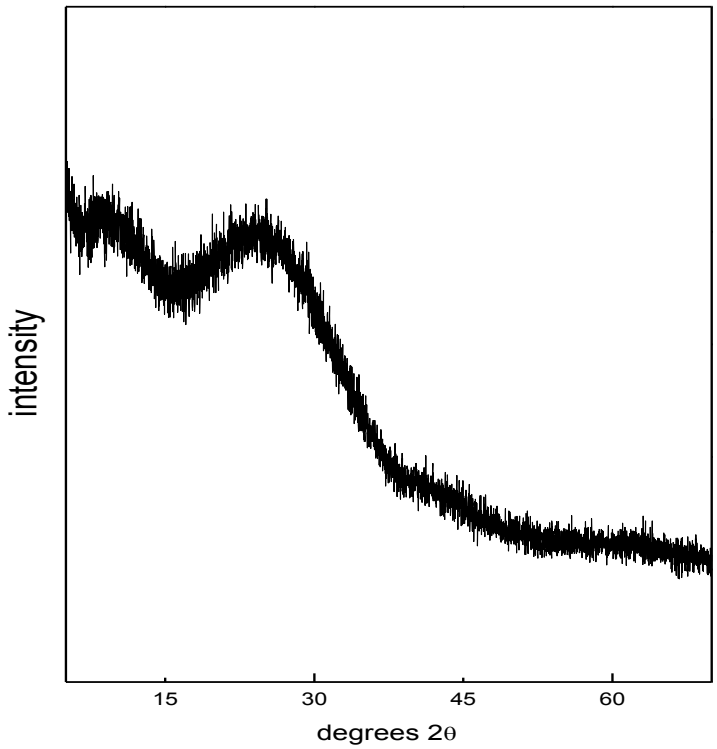


Figure 14: XRD of Ti/SiO_2 material calcinated at 400°C

(B) FT-IR spectra

The FT-IR spectra of prepared Ti/SiO_2 material are shown in figure 15. The peak observed at 972 cm^{-1} is assigned to ν (Ti-O-Si) vibrations. However, another peak appears at 1230 cm^{-1} that is assigned to ν (Si-O) vibrations.[17,32,33] The peak at 1599 cm^{-1} is due to the -OH stretching of water.[34,35] In the same spectrum a band is visible at 710 cm^{-1} which contributes to the anatase formation.[36]

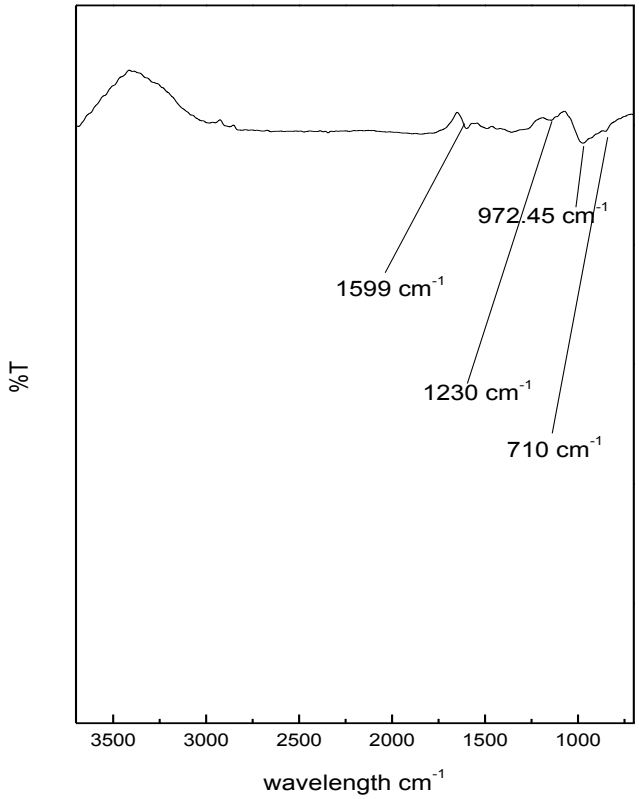


Figure 15: FT-IR of Ti/SiO_2 material

(C) SEM image

The surface morphology of the calcinated at 400°C, have been investigated by scanning electron microscopy as shown in Fig 16. The average size of the porous and irregular shaped catalyst particles by FESEM studies was found to be in the range of 4-5 μm.

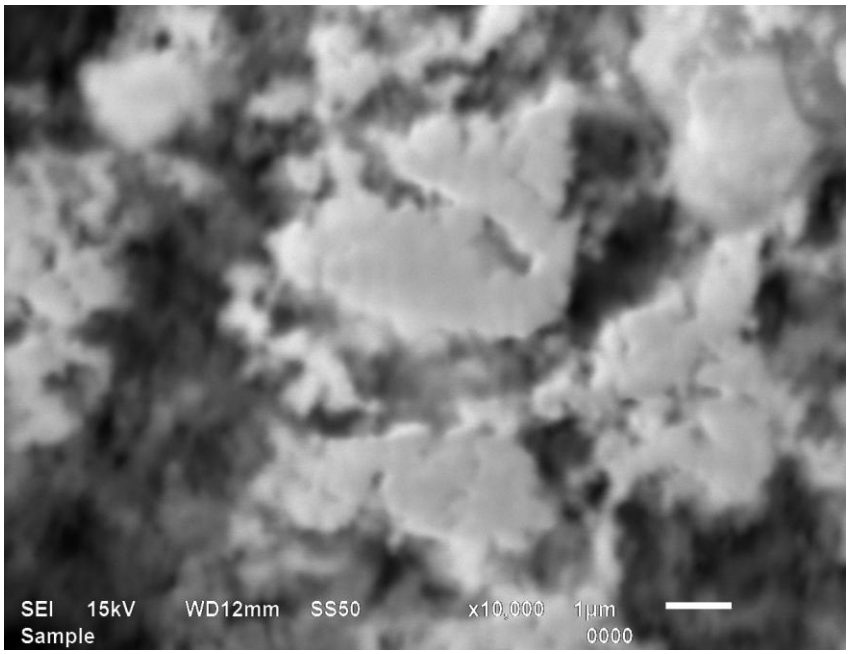


Figure 16: SEM image of Ti/SiO_2 material calcinated at 400°C

CHAPTER 5

CONCLUSIONS

CONCLUSIONS

The present work demonstrates the preparation of mesoporous molecular sieves MCM-41, MCM-48, Al/MCM-41 and Ti/SiO_2 material by using appropriate methodologies for their formation at room temperature. The prepared samples has been characterized by powder X-ray diffraction (XRD), Fourier transformed infrared (FT-IR) techniques and scanning electron microscopy (SEM). The low angle XRD patterns reveal that prepared MCM-41 has hexagonal structure whereas MCM-48 has cubic structure with 3-D pore systems. The XRD pattern of Al/MCM-41 shows the valuable existence of mesoporous network by using 1.93 wt % aluminium and the wide angle XRD data for Ti/SiO_2 material shows anatase phase of TiO_2 crystalline structure. FT-IR spectra of various mesoporous materials before calcination show peaks due to presence of organic template in the range of 3500 cm^{-1} to 1600 cm^{-1} but no peak in this region after calcination confirms the removal of organic template. The presence of Si-O-Si linkage is supported by the appearance of Si-O-Si asymmetric and symmetric stretching vibrations at 1090 cm^{-1} to 790 cm^{-1} respectively in the FTIR spectra of the same. In case of Ti/SiO_2 material presence of additional peak at 710 cm^{-1} support the formation of TiO_2 in anatase phase in hybrid material.

REFERENCES

1. J.S. Beck, C. Vartuli, W.J Roth, M.E Leonowicz, C.T Kresge, K.D Schmitt, C.T.W. Chu, D.H. Olson, Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L.; A New Family of Mesoporous Molecular Sieves Prepared with Liquid Crystal Templates. J. Am. Chem. Soc. 1992a, *114*, 10834- 10843.

2. S. Xhio Zhao; G.Lu, G. Millar, Ind. Eng. Chem. Res. 1996**,** 35, 2075-2090

3. C.T Kresge, M.E. Leonowicz, W.J Roth, J.C Vartuli, J.S Beck, Nature 359,1992, 710.

4. J.S Beck, C.T Chu, I.D. Johnson, C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, US Patent 5,108,725 to Mobil Oil Corporation, 1992.

5. P.T. Tanev, Y. Liang, T.J. Pinnavaia, J. Am. Chem. Soc.119,1997, 8616

6. Brian Melde, Brandy J. Johnson, and Paul T. Charles, Sensors, 2008, 8, 5202-5228.

7. K.S.W. Sing, D.H. Everett, R.H.W. Haul, L. Moscou, R.A. Oierotti, J. Rouquerol, T. Siemieniewska, Pure & Appl. Chem. 57,1985, 603.

8. D.W. Breck in: Zeolites Molecular Sieves, John Wiley and Sons, New York, 1974.

9. R. Szostak, Van Nostrand Reinfold, New York, 1989.

10. V. Luzzati, A. Tardieu, T.G. Krzywicki, E. Rivas, F.R. Husson, Nature, 220, 1968, 485.

11. J.C. Vartuli, C.T. Kresge, W.J. Roth, S.B. McCullen, J.S. Beck, K.D. Schmitt, M.E. Leonowicz, J.D. Lutner, E.W. Sheppard, Chapter 1, Advanced Catalysts, 1996, pp.1.

12. Q.S. Huo, D.I. Margolese, G.D. Stucky, Chem. Mater., 8, 1996, 1147.

13. J.L. Casci, Stud. Surf. Sci. Catal., 85, 1994, 329.

14. A. Sayari, Chem. Mater., 8, 1996, 1840.

15. W. Zhang, T.J. Pinnavia, Catal. Lett., 38, 1996, 261.

16. S. Qourzal Materials Science and Engineering C, 29, 2009, 1616-1620.

17. E. Rodriguez-castellon, J. Roziere, Chem. Commun.,1997, 431.

18. W. Zhang , J. Wang, P.T. Tanev, T.J. Pinnavaia, Chem. Commun.,1996,979.

19. D. Myers, Surfactant Science and Technology; VCH: New York, 1992.

20. S. Beck, J.C. Vartuli, G.J. Kennedy, W.J. Roth, S.E. Schramm, Chem. Mater. 6, 1994 1816.

21. M.E. Raimondi, J.M. Seddon, Liquid Crystals 26, 1999, 3, 305.

22. D. Kumar, K. Schumacher, C. Hohenesche , M. Grun and K.K Unge, Physicochemical and Engineering Aspects 187–188, 2001, 109–116

23. M. T. Janicke, C. C. Landry, S. C. Christiansen, D. Kumar, G. D. Stucky, and B. F. Chmelka, J. Am. Chem. Soc. 1998**,** *120*, 6940-6951

24. T.F Degnan, I.D Johnson, K.M. Keville, U.S. Patent No.5, 156, 828, 1992.

25. Anderson, Zeolites 19, 1997, 220.

26. S. Qourzal, N. Barka, M. Tamimi, A. Assabbane, A. Nounah , A. Ihlal , Y. Ait-Ichou, Materials Science and Engineering C 29, 2009, 1616–1620.

27. M. Grun, G. Lauer, K.K Unger, Adv. mater. 9(3), 1997, 254–257.

28. Xiu Mei Tai, Hong Xia wang, Xiu Qi Shi Chinese Chemical Letters Vol. 16, No. 6, pp 843-845, 2005.

29. H. Nur, L. Chin Guan, S. Endud H. Hamdan, Materials Letters 58, 2004, 1971-1974.

30. S. Holmes, V. Zholobenko, A. Thursdeld, J. Richard, C. Cundy, J. Dwyer, J. Chem. Soc, Faraday Trans, 1998, 94(14), 2025E2032

31. K. Wang, Y. Lin, M. Morris, J. Holmes, J. Mater. Chem., 2006, 16, 4051–4057.

32. M.A. Uguina, D.P. Serrano, G. Ovejero, R.V. Grieken, M. Camacho, Appl. Catal. A, Gen. 124, 1995, 391.

33. A.A. Ismail, I.A. Ibrahim, M.S. Ahmed, R.M. Mohamed, H. El-Shall, J. Photochem. Photobiol. A: Chem. 163 (2004) 445.

34. G. Martra, Appl. Catal. A: Gen. 200, 2000, 275.

35. H. Chun, W. Yizhong, T. Hongxiao, Appl. Catal. B: Environ. 30, 2001, 277.

36. I.M.M. Salvado, J.M.F. Navarro, J. Non-Crystall. Solids 147-148, 1992, 256.

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Place: Patiala
Date: 15th July, 11

Regards,
Rinipal Kaur
(RINIPAL KAUR)