CHAPTER 2

Chapter 2. Synthesis and Characterization of MCM-41 based materials

2.1 INTRODUCTION

Advanced materials are the enablers of new technologies. The present demands are better materials, new materials and cheaper materials prepared by ecofriendly routes. An important goal of materials research is the ability to design and synthesize in high yields, materials whose structures and properties can be predicted, varied and controlled. This is the challenge for the synthetic chemist by the demands of material technology. Traditional ceramic processes use high temperatures. The present demands are making use of soft chemistry routes (low temperatures) which is popularly known as “Chemie Douce” by the French. Sol-gel method of synthesis is a soft chemistry route. Advantages of materials prepared by sol-gel synthesis is high homogeneity, high purity, low temperature processing, structural control of materials formed, materials with improved or desired properties and preparation of porous materials by use of templates. A great deal of interest has been shown in the application of sol-gel chemistry in various fields of technology. A majority of the materials prepared using the sol-gel method are ceramics, refractories and glasses. Attempts to apply the sol-gel technique for the preparation of catalysts is a relatively new venture, made since the last decade.

2.2 SOL-GEL PROCESS

Concepts and Terminologies

The sol-gel process is a wet-chemical technique for the fabrication of materials, employing low temperature, starting either from a chemical solution or colloidal particles (sol for solution or nanoscale particle) to produce an integrated network (gel). In general, sol-gel process can be regarded as the preparation of the sol, gelation of the sol and removal of the solvent. The overall sol-gel process can be represented by the following sequence of transformations [1]:

Precursor → Sol → Gel → Product

Precursors are starting materials, in which the essential basic entities for further network formation are present in the correct stoichiometry. Typical precursors are metal alkoxides and metal chlorides.
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**Sol** is a colloidal suspension of particles in a liquid, the particles typically ranging from 1-100 nm in diameter. The solid particles in the colloidal phase are stable due to short-range forces such as Van der Waals attraction and surface charges.

**Gel** is a semi–rigid solid, in which solvent is contained in a network/framework of the material, which is either colloidal (essentially a concentrated sol) or polymeric. Gel is defined as a substance that contains a continuous solid skeleton enclosing a continuous liquid / fluid phases of colloidal dimensions.

In sol-gel processing, a sol of a given precursor is prepared, which involves the dissolution of the required metal ions either as alkoxides or other metallo-organic salts in a suitable solvent (alcohol) or as inorganic salts in water, which undergo hydrolysis, followed by condensation and polymerisation reactions to produce highly condensed and branched network polymers, the gel. The networking depends on the functionality of the metal. Silicon with coordination number four, forms highly branched networks [2] (Fig. 2.1a). In the gelation step, the fluid sol is transformed to a semirigid solid gel. Two types of gels are usually formed, colloidal and polymeric. Colloidal gels are formed from metal salt solutions, oxides and hydroxide sols, while polymeric gels are formed from metal alkoxide based sols. The name “sol-gel” is thus given to the process, because of the distinctive viscosity increase that occurs at a particular point in the sequence of steps. A sudden increase in viscosity is the common feature in sol-gel processing, indicating the onset of gel formation. Sol-gel process can be distinguished from precipitation by its specific property to stabilize a finely dispersed (mostly colloidal) phase in solution.

Typically, formation of a metal oxide via sol-gel route involves connecting the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges, generating metal-oxo or metal-hydroxo polymers in solution. The transformation of sol to gel takes place via hydrolysis and condensation reactions of the precursors. The hydrolysis reaction is represented taking silicon as an example:

\[
\text{Si} (\text{OR})_4 + n \text{H}_2\text{O} \rightarrow (\text{HO})_n\text{-Si} (\text{OR})_4-n + \text{ROH}
\]  

(2.1)

In case of metal alkoxide precursors, R represents an alkyl group. The metal is totally hydrolyzed when \( n = 4 \). For any other value of \( n \), partial hydrolysis
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takes place. In the condensation reaction, the two partially hydrolyzed molecules link together and liberate a small molecule such as H₂O or ROH. The general reaction is represented as:

\[(\text{OR})_{4-n} \text{Si(OH)}_n + (\text{HO})_n \text{Si(OR)}_{4-n} \rightarrow (\text{OR})_{4-n} \text{Si-O-Si(OR)}_{n-1} + \text{H}_2\text{O} \quad (2.2)\]

The condensation takes place in such a way so as to maximize the number of M-O-M bonds and minimize terminal hydroxyl groups through internal condensation. Initially monomers add to form rings, creating 3-D structures. These compact structures are formed by leaving the hydroxyl groups outside, (Fig.2.1b) that serve as nuclei for further particle growth[3], that proceeds by Ostwald ripening mechanism, a process by which small particles precipitate on relatively larger insoluble particles, indicated by arrow heads in (Fig.2.1c). As particles grow in size the number of particles decrease. The polymerization behaviour of aqueous silica via sol-gel process at different pH is presented in (Fig.2.1d).

**Fig. 2.1(a)** Highly branched networks of silicon. **(b)** Condensation reactions leading to closed ring 3D structure. **(c)** SEM showing Ostwald ripening mechanism[3]. **(d)** Polymerization behavior of aqueous silica. A = in presence of salts / acidic medium, B = alkaline medium.

**Sequential steps involved in sol-gel synthesis**
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**Hydrolysis:** It involves reaction of inorganic or organometallic precursor with water or a solvent, at ambient or slightly elevated temperature. Acid or base catalysts are added to speed up the reaction.

**Polymerization:** This step involves condensation of adjacent molecules wherein water/alcohol are eliminated and metal oxide linkages are formed. Polymeric networks grow to colloidal dimensions in the liquid (sol) state.

**Gelation:** It leads to the formation of a three dimensional network throughout the liquid, by the linking up of polymeric networks.

**Ageing:** A continuous change in structure and properties of a completely immersed gel in liquid is called ageing and represents the time between formation of the gel and removal of solvent. Aggregation of smaller polymeric units to the main network, progressively continues on ageing the gel. Solvent molecules however, remain inside the pores of the gel. Extensive ageing however, causes shrinkage of gel. Factors that affect ageing processes include temperature, time and pH of the pore liquid.

**Drying:** Here, solvent is removed at moderate temperatures (<200 °C) leaving the residue behind. During drying, the gel initially shrinks due to loss of pore fluid maintaining the liquid-vapour interface at the exterior surface of the gel. At the final stage of drying, liquid-vapour menisci recede into the gel interior[4]. The magnitude of the capillary pressure, $P_c$, exerted on the network, depends on the surface tension of the liquid, $\gamma$, the constant angle $\theta$, and the pore size, $r$: given by $P_c = 2\gamma \cos\theta/r$. If the pore size is very small, the capillary pressure will be large. The original gel network collapses due to this pressure[5]. Aging may be used to reduce the extent of collapse of the gel structure during drying. The resulting materials are identified based on drying conditions. Conventional evaporative drying such as heating a gel in an oven induces capillary pressure associated with the liquid-vapour interface within a pore, resulting in the collapse of the porous network. The sample thus obtained is called a xerogel, which has a relatively low surface area and pore volume. In supercritical drying, on the other hand, these deleterious effects are minimized due to differential capillary pressure and the resultant materials are known as aerogels. Consequently, they have high pore volumes, surface areas and low bulk densities. A third method of drying involves the freeze
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drying of the solvents at low temperature under reduced pressure. This method is similar to the lyophilization technique adopted in pharmaceutical industries and the product is called cryogel. Another method of drying is subjecting the gel to ultrasonic vibration at room temperature to remove the solvent. The gel thus obtained is called a sonogel.

Dehydration: This step is carried out between 400 °C and 800 °C to drive off the organic residues and chemically bound water. A thermal treatment firing/calcination may be performed in order to favour further polycondensation and enhanced mechanical property, when following changes, such as loss of solvents, pyrolysis of the organics, structural rearrangement and densification or crystallization are observed.

Densification: Heating the porous gel at high temperatures, leads to formation of a dense oxide product. The densification temperature depends considerably on the dimensions of the pore network, the connectivity of the pores, and surface area. Sequential steps involved in sol-gel process is presented in Fig.2.2

![Fig.2.2. Sequential steps involved in sol-gel process](image)

**Conditions for sol-gel synthesis**
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It is possible to tailor specific properties in a material by tuning the various conditions of the sol-gel process, outlined as follows:

**pH of the hydrolysis:** The pH during hydrolysis mainly decides the nature of the pores, surface area and density of the materials. In general, acid catalyzed hydrolysis gives a microporous network, while base catalyzed hydrolysis leads to the formation of a mesoporous network. The preparation of microor mesoporous materials in a neutral medium has been reported [6].

**Rate of addition of water:** The rate of addition of water during the preparation of the sol affects the rate of hydrolysis and condensation which in turn influence the texture and morphology of the gel.

**Temperature of gelation:** The rate of gelation depends on the temperature at which the sol is aged or heated for the removal of the solvent or for the facilitation of hydrolysis. If the temperature is lower, the rate of hydrolysis is slower and the particle size is relatively smaller. This results in reduced pore collapse and yields a well defined porous network.

**Aging of Gels:** Aging is the process of keeping the gels in various solutions for a period of time in order to increase the strength of the gel network, so that cracking of gels during drying can be prevented. The chemical reactions that cause gelation, continue long after gel point strengthening, stiffening and shrinkage of the network [4,7]. The composition, structure and properties of gel change during aging. The changes that occur during aging are categorized as,

- Polymerization: Increase in connectivity of the gel network by condensation reactions.
- Coarsening: Process of dissolution and reprecipitation driven by differences in solubility between surfaces with different radii of curvature.
- Syneresis: Shrinkage of the gel and the resulting expulsion of liquid from the pores.

**Drying control chemical agents (DCCAs):** The presence of DCCAs has a significant influence on the particle texture and morphology. Various DCCAs useful in controlling the porosity and bulk density are formamide, glycerol and oxalic acid.
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**Calcination temperature:** the calcination temperature is also important in controlling the pore size and density of the materials.

**Conclusions, Advantages and Disadvantages of Sol-Gel process**

The sol-gel method, thus offers the possibility to prepare solids with pre-determined structure, by varying the experimental conditions such as the choice of reagents, concentration, mode and rate of mixing, temperature, pH, ageing and drying conditions. Variation in any of these parameters yields materials with different characteristics. The preparation procedure thus affects the composition and structure, which is further reflected in the properties/performance such as porosity, surface polarity and crystallinity. The various steps involved in the sol-gel technique described above may or may not be followed. In practice, however, a modified sol-gel route is followed.

Advantages of sol-gel process include increased homogeneity, high purity, low processing temperature and high surface area of the gels or powders obtained. The inherent usefulness of this approach is largely due to the ease with which sol-gel derived materials can be prepared, modified, and processed. The mild reaction conditions afford an opportunity to incorporate various organic moieties into inorganic compounds. Furthermore, the average pore size, pore size distribution, surface area, refractive index and polarity of the resultant matrix can also be controlled and tailored by manipulations in the sol-gel processing conditions. Disadvantages of the Sol-Gel Process include, large shrinkage during processing, creation of fine pores, presences of hydroxyl groups when hydroxides are used, residual carbon in final material originating from templates, health hazards of organic solvents, and finally long processing times.

**2.3 SOL-GEL PROCESS AS APPLIED TO SILICA**

Silica gels are most often synthesized by hydrolysing monomeric, tetrafunctional alkoxide precursors employing a mineral acid or base as a catalyst. Most common tetraalkoxysilanes used in the sol-gel process are tetraethoxysilane [TEOS, (SiOC₂H₅)₄] and tetramethoxysilane [TMOS, Si(OCH₃)₄]. The sol-gel process involving silica can be described as follows,
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The hydrolysis reaction replaces alkoxide groups with hydroxyl groups. Subsequent condensation reactions involving the silanol groups produce siloxane bonds and the by-products, alcohol or water. Under most conditions, condensation commences before hydrolysis is complete. Since water and alkoxy silanes are immiscible, a mutual solvent such as alcohol is normally used as a homogenising agent. In order to reduce the reactivity of the alkoxide precursor, organic functional groups are introduced into the siloxane network. This type of alkoxide precursors are known as organoalkoxysilanes.

The surface and structural characteristics of the silica gels are affected by various parameters that control the rate of hydrolysis and condensation and these can be summarized into three categories[8]:

Composition: Type of starting materials, quantity of water, catalysts and solvents.

Reactions (up to gel formation): Rate of mixing, reaction temperature and gelation schemes.

Process variables (after gel formation): Type of dehydration, drying temperature and heating.

Factors affecting silica gel synthesis are mole ratio of H₂O to alkoxides and pH values that play a significant role in determining reaction rates, morphology and composition. Changes in pH values during the sol preparation stage significantly affects the appearance of sample, porosity, density, viscosity, gelation time, activation energy, surface area, pore volume, and pore size distribution. Increase in the gelation temperature could make the gelation process shorter, while increase in drying temperature would cause the pore diameter to become bigger. Intermediate conditions produce structures intermediate to these extremes.
2.4 SOL-GEL SYNTHESIS AS APPLIED TO ZEOLITES

The factors that influence the synthesis of crystalline zeolite are summarized as follows:

- Composition of the reaction mixture.
- Nature of reactants.
- Initial and final pH of the system.
- Temperature of the process and its variation with time (if any).

  - Ambient: 25 to 60 °C
  - Low: 90 to 120 °C
  - Moderate: 120 to 200 °C
  - High: 250 °C or higher

- Time allowed for the reaction to take place, including the calcination time.
- Mixture, whether homogeneous or heterogeneous.
- Seeding.
- Template molecules (if any).
- Other factors:
  - Aging
  - Stirring (fast/slow) (time)
  - Nature of mixing
  - Order of mixing

**Composition of the Reaction Mixture:**

The composition of the reaction mixture is one of the most important factors governing the product properties, which includes:

- Silica to alumina ratio.
- Hydroxyl, ion concentration.
- Inorganic cations.

The ratio of $\text{SiO}_2 / \text{Al}_2\text{O}_3$ in the gel phase decides the framework composition of the zeolite. The hydrophobic / hydrophilic nature of zeolite is also affected by this ratio as aluminium is hydrophilic and silicon is hydrophobic. Also, high aluminium contents give higher acidic sites, which are useful for many applications. Zeolites with higher silica / alumina ratio are used for catalytic applications in cracking and isomerization. As the aluminium content is...
increased the acid resistance & thermal stability of the zeolite reduces. These effects can be summarized as follows:

Increasing the silica / alumina ratio affects following physical properties of the zeolite:

- Increases acid resistance.
- Increases thermal stability.
- Increases hydrophobicity.
- Decreases affinity for polar adsorbents.
- Decreases cation content.

Decreasing the silica / alumina ratio affects following physical properties of the zeolite:

- Increases hydrophilicity.
- Increases cation exchange properties.
- Decreases the pore size for same numbered ring, as aluminium has lower atomic radius than silicon.

Hydroxide ion concentration:

It functions as structure director through control of the degree of polymerization of silicates in solution. OH\(^{-}\) ion modifies the nucleation time by influencing transport of silicates from the solid phase to solution. It enhances the crystal growth and controls the phase purity. In a study\(^{[9]}\) it was found that the OH\(^{-}\) / Si ratio influences the pore size, i.e. higher the ratio, wider were the pores.

Role of Inorganic Cations:

Inorganic cations are added to the reaction mixture, to induce crystallization of specific zeolite structures, that could not have been formed in their absence. These cations are used in the zeolite synthesis for following reasons:

- They act as structure directing agents.
- They balance the framework charge.
- They govern the morphology of the zeolite.
- They affect the crystal purity.
- They also affect the product yield.

Due to their charge and their orientation in the reaction mixture, inorganic cations alter the pore sizes of the zeolites. Most commonly used cations are alkyl ammonium ions such as tetramethyl ammonium (TMA),
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tetraethyl ammonium (TEA), etc. Apart from silica to alumina ratio and pH, the amine concentration is also a very important variable [10].

Zeolite synthesis is described in two steps: nucleation and crystallization. Nucleation is a process where small aggregates of precursors give rise to germ nuclei (embryos), which become larger with time. The rate of nucleation of a new phase from a melt increases by decreasing the temperature of the system. Crystallization starts by involving nuclei and ingredients from the solution mixture. The deposition on a seed or stable nucleus increases with the extent of stirring and temperature. The yield of the crystals increases at a rate proportional to total free external surfaces of the crystal.

Crystallization can be split into four stages:

- Formation of water icebergs. These icebergs are ring-like structures of water molecules, interconnected by hydrogen bonding.
- Depolymerization of the condensed large molecules of the precursors then takes place.
- These depolymerized molecules start orienting around the water icebergs, thus forming the nuclei.
- These nuclei form terminated tetrahedral. resulting into crystalline structures.

**pH of the Reaction Mixture**

The zeolite synthesis via sol-gel process is carried out in alkaline pH (> 10). Crystal formation is accompanied by increase in pH indicating that SiOH in colloidal state is incorporated in the framework in the form of SiO₂. Since SiOH is acidic in nature, the crystallization is accompanied by increase in pH. Further, the pH of the system is also very important for stabilizing the sol and control of the particle size.

**Role of additives**

Addition of colloidal particles e.g. Polystyrene causes organization of the pores. Polystyrene acts as a template as well as nucleating agent.
2.5 SOL-GEL PROCESS USING TEMPLATES

Introduction

One of the important modified routes in sol-gel process involves use of templates. Templates are structure directing agents, that find applications in synthesis of porous materials with tailor made dimensions. They are organic molecules (singular or assembly) around which the main structure is built up – a process very similar to a casting process. Template synthesis began from using quaternary alkyl ammonium ions - with alkyl chain length containing 10-20 carbons.

Templates, when used at optimum concentration, referred to as Critical Micelle Concentration (CMC), orient themselves to form an assembly with the polar head groups pointing outside, around which the anions orient to form a network. The layers of inorganic materials seem to distort and crosslink around the polar head groups to form a new mesoporous structure. The driving force for this layer folding, is most likely the ion pairing between the positively charged head groups and the negatively charged inorganic components. The template can subsequently be removed from the system, either by solvent extraction method or by calcination, to obtain finished product with predetermined pore size and structure. Excellent up-to-date reviews on the use of various organic templates and the mechanism of structure directing agents are available in the literature [11-13].

Concepts of templating

The main concept of obtaining well defined mesostructures is to use a surfactant templated polymerization instead of an uncontrolled reaction. In general, the Lyotropic (i.e. amphiphilic) molecules of the surfactant form a liquid crystal by aggregation in aqueous solution[14,15]. Formation of the liquid crystal matrix is strongly dependent on the conditions in the solution and the structure of the liquid crystal is the so called mesostructure. Important parameters for the mesophase formation are, the temperature, concentration and pH- value of the solution. Depending on these conditions, the structure of the mesophase can be for example ordered with spherical, cylindrical, lamellar or cubic phases or disordered.
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In the broadest sense, a template may be defined as a central structure about which a network forms in such a way, that removal of the template creates a cavity with morphological and/or stereochemical features related to those of the template[16]. A general template approach is illustrated in Fig. 2.3, where primary structural units are organized around a molecular template and solidified to form a matrix.

![Fig. 2.3 Schematic of the organic template approach showing the incorporation and removal of the template.](image)

The fidelity of the imprint created by template removal depends on several factors:

- The nature of the interaction between the template and the embedding matrix.
- The ability of the matrix to conform to the template.
- The relative sizes of the template and the primary units used to construct the matrix. Examples of single molecules used as templates are ethylamine(EA), isopropylamine(IPA), ethylmethylamine (EMA), diethylamine (DEA), n-propylamine(nPA), ethylenediamine (en) tetramethyl ammonium(TMA), and tetraethyl ammonium(TEA). Surfactants/assemblies used as templates are cetyl trimethyl ammonium bromide (CTABr), cetyl trimethyl ammonium chloride (CTACl), cetyl pyridinium bromide (CPBr), and cetyl pyridinium chloride(CPCI).

Surfactants are amphiphilic molecules which consist of a hydrophilic, polar head group and a hydrophobic, non-polar tail. Due to their amphiphilic nature, surfactant molecules have a high affinity towards surfaces and interfaces, thereby the term “surfactant” emerges which is an abbreviation for “surface active agent”. Surfactants may be classified into four different groups, depending on the nature of the polar head group: anionic surfactants, cationic surfactants, zwitterionic surfactants and non-ionic surfactants[17]. In aqueous solutions, the surfactants associate into aggregates called micelles, if
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The concentration is above the critical micelle concentration (CMC). If the concentration is increased even further, or a polar additive is added, the surfactants self-assemble into liquid crystalline mesophases.

The geometry of the surfactant aggregates formed in solution is dependent upon the shape of surfactant and its concentration, which is expressed by the term surfactant packing parameter:\[ [v/v_a] \] where \( v \) is the volume of the surfactant tail, \( a \) is the effective head group area and \( l \) is the length of the extended surfactant tail, Fig. 2.4a.

Due to variations in size of different types of surfactant tails and head groups, this ratio will vary for different types of surfactants. The relative sizes of the tail and head group therefore govern the optimal way of packing the surfactants together into aggregates of different geometry,\[ [17, 19] \] as shown in Fig. 2.4b. If the packing parameter is below 1/3, only spherical micelles exist in the solution. An increase in concentration causes these spherical micelles to organize themselves in the solution, which creates a three-dimensional, cubic ordering. A \( v/v_a \) ratio above 1/3 creates aggregates with a rod-like shape. If the concentration of the surfactants is sufficiently high, these rod-shaped micelles assemble into a hexagonal array, thereby creating a hexagonal liquid crystal.
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Fig. 2.4(a) Visualization of the geometrical considerations for the surfactant packing Parameter [19]. (b) Different liquid-crystalline phases as a function of the surfactant packing Parameter [17]. (c) Curvatures of different types of surfactant surfaces.

For $v/a_l = 1$ there is a balance between sizes of the head group and tail, which causes the surfactants to form planar aggregates with a sheet-like, bilayer structure. With sufficient concentration, three-dimensional liquid crystals with lamellar or bicontinuous cubic structures are created. If $v/a_l$ is increased above 1, the surfactants form reversed “water-in-oil” systems. The value of the packing parameter may be influenced by the addition of cosolutes in the surfactant solution[17,19]. Hydrophobic molecules dissolve in the interior of the micelles, causing an increase of ‘$v$’. Short-chained alcohols reside in the palisade layer in the micelles, thereby decreasing ‘$a$’ and increasing ‘$v$’. Electrolytes in the solution adsorb on the micelle surface (of ionic surfactants), which decrease $a$ due to screening of the repulsion between the head groups. For non-ionic surfactants, the polarity and thereby the solubility of the head group is dependent upon temperature. An increase in temperature decreases this polarity, which decreases ‘$a$’. Introduction of other types of surfactants into the solution also affects the packing parameter. The surfactants interact with each other and form mixed micelle systems, which has an average packing parameter.

The surface area of surfactant mesophases is highly dependent upon the curvature of the surface, as visualized in Fig.2.4c. A convex surface has a higher surface area than a concave surface, with the planar surface in between. For ionic surfactants, the surface of the aggregates is charged. The charge density of a charged surface is defined [20] as: $\sigma = Q / A$ where $\sigma$ is the charge density, $Q$ is the surface charge and $A$ is the surface area. Fig.2.4c shows that concave surfaces have higher charge densities than convex surfaces, due to the lower surface area. The different liquid-crystalline structures shown in Fig.2.4b have different surface curvatures and thereby different surface charge densities. It can be seen that the surface charge density of the surfactant mesophases increases with increasing packing parameter, due to the closer packing of the charged head groups.
2.6 THE FORMATION OF MESOPOROUS STRUCTURES

Introduction

A number of models have been proposed to explain the formation of mesoporous materials and to provide a rational basis for the various synthetic routes followed. All these models are proposed on the basis of structure directing ability of surfactants or templates in solution. Surfactants with hydrophilic head groups and hydrophobic tail within the same molecule get self-organized so as to minimize the contact with incompatible ends. The principal difference amongst various synthetic routes is the way in which the surfactants interact with inorganic species. Earlier it was thought that the formation of these materials is a result of electrostatic complementary between charged surfactant and inorganic species. But later the mesostructured materials have been prepared by exploring other possible interactions other than electrostatic pathways. The formation of these materials can be viewed alternatively as the interface chemistry between the surfactant and inorganic species. The mesoporous materials can be prepared by exploiting ionic, hydrogen bonding as well as covalent bonding interactions. Different synthesis mechanisms have been proposed to explain the formation of mesoporous materials. A few of them are described below:

Liquid Crystal Templating (LCT) Mechanism

There are three main liquid crystalline phases with hexagonal, cubic and lamellar structures. Because of the similarity between the different M41S phases MCM-41 hexagonal, MCM-48-cubic, MCM-50-lamellar and known liquid crystal phases, the first mechanism proposed for the synthesis of these materials was the liquid crystal templating mechanism [14,21-23]. In aqueous solution, surfactant molecules exist as randomly dispersed monomolecules at low concentrations. With increasing concentration, the surfactant molecules aggregate with their hydrophobic tails together exposing their polarheads to the aqueous solution to reach a minimum energy configuration and thus formspherical micelles decreasing the system entropy. The lowest concentration at which monomolecules aggregate to form spherical isotropic micelles is called critical micellie concentration (CMC1). There exists a
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second critical concentration (CMC2) corresponding to the further aggregation of spherical into cylindrical or rod-like micelles. The hexagonal phase is the result of hexagonal packing of cylindrical micelles, the lamellar phase corresponds to the formation of surfactant bilayers and the cubic phase may be regarded as an intercontinuous structure. The structure of the mesophase depends on the composition of the mixture, the pH and the temperature [24].

Two possible pathways have been proposed [14] for the LCT mechanism which are schematically shown in Fig. 2.5. Pathway-1 is a surfactant controlled pathway, in which the surfactant arrays, prior to the condensation of framework materials. In this pathway, it is considered that first there is a formation of the surfactant hexagonal liquid-crystal phase around which the growth of the inorganic materials is directed. The surfactant micelles aggregate to form hexagonal arrays of rods. Silicate anions present in the reaction mixture interact with the surfactant cationic head groups. Condensation of the silicate species leads to the formation of an inorganic polymer.

**Fig. 2.5** Possible mechanistic pathways for the formation of MCM-41: (1) liquid crystal phase initiated and (2) silicate anion initiated [14].

Pathway-2 is a silicate controlled mechanism, in which the silicate species condense continuously around micelles, as they form rods and pack into a hexagonal structure. This is thought of as a cooperative self assembly pathway. In this pathway, it has been proposed that the randomly ordered rodlike micelles interact with silicate species by coulombic interactions in the reaction mixture to produce approximately two or three monolayers of silicate around the external surfaces of the micelles. These randomly ordered
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composite species spontaneously pack into a highly ordered mesoporous phase with an energetically favourable hexagonal arrangement, accompanied by silicate condensation. With the increase in heating time, the inorganic wall continues to condense. The absence of hexagonal liquid crystalline mesophases, either in the synthesis gel or in the surfactant solution (used as template) it was concluded that formation of MCM-41 phase is possibly via pathway 2 rather than pathway 1.

Transformation mechanism from lamellar to hexagonal phase

It has been proposed that[24-26] in a surfactant/silicate aqueous mixture with relatively low pH, low degree of polymerization of silica species, and low temperatures, small silica oligomers (three to eight silicon atoms) interact with surfactant cations by coulombic interactions at the interfaces forming multidentate binding between them. These subsequently polymerize to form larger ligands, enhancing the binding between the surfactant and silicate species. These surfactant silicate multidentate ligands lead to a lamellar biphase governed by the optimal surfactant average head group area (A). As the polymerization of silicate species proceeds, the average headgroup area of surfactant assembly increases due to the decrease in the charge density of larger silicate layers and ultimately results in the hexagonal mesophase precipitation(Fig.2.6).

Fig. 2.6 Transformation mechanism from lamellar to hexagonal phase [25].

Folded Sheet Mechanism

Yanagisawa et al. [27] and Inagaki et al.[28,29] synthesized crystalline mesoporous silicate andaluminosilicate materials designated as FSM-16 (Folded Sheet Mesoporous Materials). They proposed a folded sheet mechanism (Fig. 2.7) for the formation of mesostructures derived from kanemite (layered silicate). The surfactant cations intercalate into the bilayers of kanemite by ion-exchange process. The transformation to the hexagonal
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phase occurs during hydrothermal treatment by condensation of silanols. MCM-41 and FSM-16 are similar but show slightly different properties in adsorption [22] and surface chemistry [30].

![Folded sheet mechanism diagram]

**Fig. 2.7 Folded sheet mechanism** [29]

### 2.7 GENERALIZED LCT MECHANISM

Based on the specific type of electrostatic interaction between a given inorganic precursor “I” and surfactant head group “S” various synthesis routes have been evolved as presented in scheme 2.1.

<table>
<thead>
<tr>
<th>Surfactant Type</th>
<th>Inorganic precursor Type</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct pathways (Ionic interactions)</td>
<td>Cationic + Anionic</td>
<td>$S^+I^-$</td>
</tr>
<tr>
<td></td>
<td>Anionic + Cationic</td>
<td>$S^+I^+$</td>
</tr>
<tr>
<td>Mediated pathways (Ionic interactions)</td>
<td>Cationic + Cationic</td>
<td>$S^+X^+I^+$</td>
</tr>
<tr>
<td></td>
<td>Anionic + Anionic</td>
<td>$S^+M^+I^-$</td>
</tr>
<tr>
<td>Neutral pathways</td>
<td>Neutral + Neutral</td>
<td>$S^O^O^O$</td>
</tr>
<tr>
<td>Ligand assisted pathways (Covalent bonding)</td>
<td>Neutral + Neutral</td>
<td>$S-L$</td>
</tr>
</tbody>
</table>

**Scheme 2.1 Possible synthetic routes for mesoporous materials**

**Direct pathways:**

In the case of direct pathway, surfactants are directly bonded to inorganic precursors through electrostatic interactions. So far, most of the materials have been prepared with cationic surfactants like CTABr/CTACl. Based on the original LCT mechanism, which involves the
anionic silicate species and cationic quaternary ammonium surfactant, it could be categorized as the S\(^+\)I\(^-\) pathway. However, a variety of surfactants can serve the purpose. In all these cases, control of pH is critical. Various materials have been prepared with S\(^+\)I\(^-\) and S\(^-\)I\(^+\) pathways [14,31-35].

**Mediated Pathways:**

Here charge interaction pathways are S\(^+\)I\(^+\), S\(^-\)X\(^-\)I\(^+\) (where x is a counter anion) and S\(^-\)M\(^+\)I\(^-\) (where M is metal cation). By operating well below the isoelectric point of silica under acidic conditions (pH ~2), the silicate species are cationic. In this case the halide ions (X\(^-\)) act as mediators. In charge reversed situation, where the surfactants and inorganic species are negatively charged the metal ion M\(^+\) (where M = Na\(^+\) or K\(^+\)) act as mediators. By maintaining higher pH conditions, it is possible to prepare mesoporous materials by S\(^-\)M\(^+\)I\(^-\) pathway through metal ion mediation. Materials prepared by S\(^+\)X\(^-\)I\(^+\) and S\(^-\)M\(^+\)I\(^-\) pathways are reported [33-35].

**Neutral Pathways:**

Tanev and Pinnavaia [36] proposed a neutral templating mechanism based on hydrogen bonding interactions (S\(^\circ\)-I\(^\circ\)) between neutral primary amine (S\(^\circ\)) which acts as template and neutral inorganic precursors (I\(^\circ\)). Hydrolysis of tetraethylorthosilicate in an aqueous solution of primary amine yields the neutral Si(OCH\(_2\)\(_2\))\(_4\)-X(OH)\(_x\) species which then binds through H-bonding to the surfactant head group. This leads to the formation of rod-like micelles. Further, hydrolysis followed by condensation, leads to Hexagonal Mesoporous Silica (HMS). The neutral templating route provides several advantages over materials prepared by electrostatic pathways, mainly the synthesis can be carried out at room temperature and the surfactant can be removed by extraction with ethanol.

Even though this process, S\(^\circ\)I\(^\circ\) offers the practical advantage of facile template recovery by non-corrosive solvent extraction or evaporation methods, these surfactants have some limitations. Neutral amines are costly and toxic and not ideally suitable for the industrial scale preparation of materials. So there exists a need to think of a process with low cost and environmentally compatible neutral templating route. Polymeric polyethylene oxide (PEO) surfactants have been used to prepare these materials which are
Chapter 2. Synthesis and Characterization of MCM-41 based materials

relatively inexpensive and biodegradable. The main advantage of using polymeric surfactants is the requirement of the lower concentration of the surfactant. These surfactants form spherical to flexible rod or worm like micelles at critical concentrations approximately one hundredth of those required for ionic surfactants [37]. It is also observed that polymeric polyethylene oxide tri-block copolymer is a promising surfactant. In the presence of suitable solvents or combination of solvents these PEO/PPO/PEO tri-block copolymeric surfactants arrange into different lyotropic phases.

Ligand Assisted interactions

By a different synthetic approach [38], it is possible to prepare mesoporous materials through covalent interactions. Instead of relying on charge interaction, the surfactants were pretreated with the metal alkoxides in the absence of water to form metal-ligand covalent bonded complexes. High quality materials are formed by the use of amine surfactants, due to the strong affinity for nitrogen-metal bond formation between surfactant head group and the inorganic precursor. In this ligand assisted templating approach, the control of the mesostructure was found possible by adjusting the metal/surfactant ratio, and it has been established that the M41S family of mesoporous materials can be prepared through this approach. Mesoporous materials prepared by various methods are presented in Table 2.1.

2.8 REMOVAL OF TEMPLATE

Once the framework condenses around the micellar rods, a nonporous solid is formed. To produce the porous species, the template must be removed from the framework. The method of template removal depends on the desired morphology and the thermal stability of the synthesized compound. MCM-41 shows reasonable thermal stability. As such, the surfactant template is removed by calcination. In this context, calcination refers to simply heating the sample sufficiently to burn out the organic phase and leave behind the porous framework [38,39]. The calcination has to be done in the flow of inert gases at the initial stages followed by the flow of air. This is to maintain the crystallinity of the material. The template can also be removed by washing the as synthesized material with extracting solvents.
### Chapter 2. Synthesis and Characterization of MCM-41 based materials

#### Table 2.1 Summary of Mesoporous materials prepared by various methods [14,31-38]

<table>
<thead>
<tr>
<th>Class of Materials</th>
<th>Type</th>
<th>Preparation Method</th>
<th>Observed phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>M41S</td>
<td>MCM-41</td>
<td>$S^+ I^-$</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>MCM-48</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCM-50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T-M41S (T=Transition metals)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SBA</td>
<td>SBA-1</td>
<td>$S^+ X^- I^+$</td>
<td>Cubic</td>
</tr>
<tr>
<td>SBA-2</td>
<td></td>
<td></td>
<td>3D-Hexagonal</td>
</tr>
<tr>
<td>SBA-3/APM</td>
<td></td>
<td></td>
<td>MCM-41 Like</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Hexagonal</td>
</tr>
<tr>
<td>SBA-11</td>
<td></td>
<td></td>
<td>Cubic</td>
</tr>
<tr>
<td>SBA-12</td>
<td></td>
<td></td>
<td>3D-Hexagonal Material</td>
</tr>
<tr>
<td>SBA-14</td>
<td></td>
<td></td>
<td>Lamellar</td>
</tr>
<tr>
<td>SBA-15</td>
<td></td>
<td></td>
<td>2D-Hexagonal</td>
</tr>
<tr>
<td>SBA-16</td>
<td></td>
<td></td>
<td>3D-Cubic cage structure</td>
</tr>
<tr>
<td>T-SBA (T=Ti,V,Mn,Mo,Cr,Zr)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MSU</td>
<td>MSU-1 Silica</td>
<td>$N^- I^-$</td>
<td>Worm-like disordered</td>
</tr>
<tr>
<td></td>
<td>MSU-2 Silica</td>
<td></td>
<td>Worm-like disordered</td>
</tr>
<tr>
<td></td>
<td>MSU-3 Silica</td>
<td></td>
<td>Worm-like disordered</td>
</tr>
<tr>
<td></td>
<td>MSU-V</td>
<td></td>
<td>Lamellar</td>
</tr>
<tr>
<td></td>
<td>Ti-MSU- Silica</td>
<td></td>
<td>Worm-like disordered</td>
</tr>
<tr>
<td></td>
<td>Zr-MSU- Silica</td>
<td></td>
<td>Worm-like disordered</td>
</tr>
<tr>
<td></td>
<td>Nb-TMS1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ta-TMS1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TMS</td>
<td>Nb-TMS2</td>
<td></td>
<td>Hexagonal</td>
</tr>
<tr>
<td></td>
<td>Nb-TMS3</td>
<td></td>
<td>Hexagonal</td>
</tr>
<tr>
<td></td>
<td>Nb-TMS4</td>
<td></td>
<td>Cubic Layered</td>
</tr>
<tr>
<td>PHTS</td>
<td>PHTS</td>
<td>$S^+ X^- I^+$</td>
<td>Analogue to SBA-15</td>
</tr>
<tr>
<td>MCF</td>
<td>MCF</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Swelling agent added to Synthesis of SBA-15</td>
<td></td>
<td>Sponge-like foam with 3D-structure with large uniform spherical cell</td>
</tr>
<tr>
<td>HMS</td>
<td>T-HMS (T=Si,V,Al,Ga,Fe,Cr,Mo)</td>
<td>$S^- I^+$</td>
<td>Hexagonal</td>
</tr>
</tbody>
</table>

**MSU**: Michigan State University  
**HMS**: Hexagonal Mesoporous Silica  
**PHTS**: Plugged Hexagonal Templated Silica  
**MCF**: Meso Cellular Form  
**SBA**: Santa Barbara Amorphous or Santa Barbara Acid Material  
**TMS**: Transition Metal Oxide Mesoporous Molecular Sieves  
**M41S**: Mobil Composition of Material or Mobil Composition of Matter
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Some of the more effective solvents are ethanol and supercritical CO₂. When using supercritical extraction (SCE), polar modifiers are added to enhance the extraction capability of the supercritical fluid. Commonly used modifiers are dichloromethane (DCM) and methanol [40]. In the case of materials prepared through hydrogen bonding interactions, the removal of the template can be achieved either by repeated extraction with ethanol or by calcination.

Each method of template removal has advantages and disadvantages. Standard calcination programs are effective at removing all of the template, but the high temperatures generally cause some loss of long range order and shrinkage of pores within the MCM structure. Extractions with ethanol are easy to perform at room temperature but are not as effective at completely removing the template. Supercritical extractions are extremely efficient at removing surfactants. It is a more environmentally benign extraction method as the surfactant can be recovered for use in subsequent synthesis as opposed to being burned to oxidation products in typical calcinations. Due to the interesting properties of supercritical fluids, SCE does not induce structural degradation whereas pore shrinkage and some loss of long-range order arise in thermal calcinations [40]. Unfortunately, supercritical extraction is expensive and difficult to perform.

2.9 SYNTHESIS STRATEGIES AND CHARACTERIZATION METHODOLOGIES - A LITERATURE SURVEY

Synthesis strategies of Siliceous MCM-41 - A Literature Survey

The discovery of MCM-41, has attracted considerable attention due to large and uniform pore size distribution, high surface area (>800 m²/g) and distinct adsorption properties [21]. Siliceous MCM-41 when synthesized is chemically inert in which catalytic activity has to be imparted. It is essential that the MCM-41 thus synthesized should be hydrothermally stable for functionalizing, after which it can be held at relatively higher temperatures and even under harsher conditions, which is generally prevalent when used in industries. In addition, if one needs to scale up for producing larger quantities, the synthesis has to be simple, lesser energy demanding, cost effective and
environment friendly, like handling and usage of appropriate concentration of chemicals without much of secondary wastes.

Several synthesis methods have been proposed and successfully used to synthesize mesoporous MCM-41 molecular sieves [24,41-44]. These materials are normally synthesized by hydrothermal procedures and their structures are obtained from amorphous inorganic silica walls around surfactant molecules. It is now well documented in literature that the formation of mesostructures is influenced by surfactant concentration, pH, presence of co-surfactant, and its concentration and temperature [45-52].

Generally siliceous MCM-41 materials are synthesized from gels with surfactant/silica molar ratio of more than 0.12 [45-48, 53-59] and involves hydrothermal treatment of precursor gel in the temperature range between 60–150°C for a long time (1–6 days) in presence of quaternary ammonium surfactants, CₙH₂n⁺ (CH₃)₃N⁺, with different alkyl chain lengths (n = 8–18), using sodium silicate or tetraalkylorthosilicate as sources of silica [15,48,50,53-56]. Siliceous MCM-41 has also been synthesized under refluxing [53,57] and microwave irradiation [58]. Attempts have been made to synthesize siliceous MCM-41 materials under ambient conditions [60-68]. Voegtlin et al. [64] have prepared highly ordered MCM-41 at room temperature in 1 h; however, stability above 873 K has not been reported. Different strategies have been employed to improve thermal and hydrothermal stability of these materials, such as synthesis of materials with thicker pore wall under hydrothermal condition by using low surfactant to silica molar ratio in the range of 0.06 to 0.1 [56], by addition of salts in the synthesis gel before or during hydrothermal crystallization [69-72] and/or intermittent pH adjustment with acid during hydrothermal treatment [71,73] and using highly condensed silica source such as fumed silica [74,75] and calcined MCM-41 silica [76]. Cheng et al [77] have synthesized MCM-41 using fumed silica at 438 K in 48 h with pore wall thickness of 2.68 nm and showed improved thermal stability. Kumar et al [78] have synthesized MCM-41 analogue at room temperature using hexadecylamine as templating agent that exhibited improved stability. However, most of the approaches suffer process difficulties.
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in large scale preparation, as the synthesis involves longer crystallization time at higher temperatures (100°C-150°C).

A highly ordered mesoporous siliceous MCM-41 has been synthesized in, using a simple synthesis methodology at room temperature with surfactant to silica ratio 0.1, using sodium silicate as silica source and CTAB as structure directing agent, adding silicate solution to the surfactant solution at a controlled rate, resulting in synthesis of a well crystalline MCM-41, with improved thermal and hydrothermal stability at room temperature in less than 3 h [79].

Modified MCM-41 materials

As already mentioned in chapter I, MCM-41 based materials have negligible catalytic activity due to framework neutrality. MCM-41 can be used as solid acid catalyst by generation of acid properties in MCM-41 that enhances its practicability and exhibit remarkable catalytic performance.

A purely siliceous framework is electronically neutral. When lattice Si⁴⁺ cations are replaced by Al³⁺ cations, pure siliceous MCM-41 loses neutrality. The negatively charged framework is balanced by Na⁺ ions present in the system. In order to form acidic mesoporous materials, ion exchange with ammonium nitrate is carried out, followed by thermal decomposition of the NH₄⁺ cations into protons and ammonia. The Brønsted acid sites are protons, loosely attached to lattice oxygen atoms in the vicinity of aluminium. With increased Al³⁺ incorporation in the MCM-41 lattice the acidity increases. Thus, by incorporation of Al³⁺ in the MCM-41 framework, material with inherent acidity is obtained, generally entitled as Al-MCM-41.

Heteropoly acids (HPAs) have proved to be the alternative to traditional mineral acid catalysts due to both strong acidity and appropriate redox properties. However, limitations for HPAs to be used as solid acid catalysts are low thermal stability, low surface area (1-10 m²/g) and difficulty in separation from reaction mixture due to their high solubility in polar solvents. For HPAs to be effective as catalysts, they should be supported on a carrier with a large surface area. Owing to a very large surface area and a uniform large pore size, the MCM-41 materials can act as excellent supports that provide an opportunity for HPAs to be dispersed over a large surface area.
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and hence increased catalytic activity. Further, such mesoporous materials, which have relatively small diffusion hindrance, can aid the easy diffusion of bulky organic molecules in and out of their mesopores. Thus, heteropoly acids (HPAs) supported onto MCM-41 by process of anchoring and calcination yields material with induced acidity [80,81].

Characterization Methodologies - A Literature Survey

Characterization of MCM-41

As the most investigated member of the M41S family, MCM-41 provides an excellent example in characterizing mesoporous materials. MCM-41 has a honeycomb structure that is the result of hexagonal packing of unidimensional cylindrical pores. Reliable characterization of the porous hexagonal structure requires the use of three independent techniques [82]: X-ray diffraction (XRD), transmission electron microscopy (TEM) and adsorption analysis.

The XRD pattern of MCM-41 shows typically three to five reflections between 2θ = 2° and 5° (Fig. 2.8), although samples with more reflections have also been reported [83,84]. The reflections are due to the ordered hexagonal array of parallel silica tubes and can be indexed, assuming a hexagonal unit cell as (100), (110), (200), (210) and (300). Out of the XRD peaks exhibited in the low angle region for mesoporous phase, the most intense peak is the (100) reflection. The powder pattern is the fingerprint of the molecular sieve structure and can be ascertained by comparing with the standard pattern for the molecular sieves under investigation. Since the materials are not crystalline at the atomic level, no reflections at higher angles are observed. Moreover, these reflections would only be very weak in any case, owing to the strong decrease of the structure factor at high angles. By means of XRD it is not possible to quantify the purity of the material. Samples with only one distinct reflection have also been found to contain substantial amounts of MCM-41. It is reported that even when the hexagonal pore structure contains a large number of defects, a hexagonally indexable three-reflection pattern can be calculated [85].

Transmission Electron Microscopy (TEM) is used to elucidate the pore structure of mesoporous molecular sieves [14,22,35]. It provides
topographic information of materials at near atomic resolution. However, the exact analysis of pore sizes and thickness of the pore walls is very difficult and not possible without additional simulations because of the ‘focus’ problem. Chen et al [86] have reported that the thickness of MCM-41 depends strongly on the focus conditions, and careful modelling is necessary for precise analysis. More than one model with a hexagonal array of large cylindrical pores with thin walls gives a similar XRD pattern, but TEM gives a direct, precise and simultaneous measurement of the pore diameter and pore thickness. HRTEM can be successfully used to examine the microstructural feature of mesoporous molecular sieves [87,88]. In addition to structural characterization, it can also be used to detect the location of metal clusters and heavy cations in the framework [88]. Fig. 2.9 shows a TEM image of the hexagonal arrangement of uniform, 4 nm sized pores in a sample of MCM-41. Most MCM-41 samples not only show ordered regions but also disordered regions, lamellar and fingerprint-like structures [87]. The existence of a lamellar phase after calcination is unlikely, because silicate layers are too distant from one another to preserve the spacing in the silicate organic phase and collapse without additional post-treatments.

Scanning electron microscopy (SEM) is also used to study the morphology of the material. It also gives an idea about the changes in shape, size and surface that occur in a used material.

Adsorption of probe molecules has been widely used to determine the surface area and to characterize the pore size and pore-size distribution of MCM-41 type materials.

The Braunauer-Emmett-Teller (BET) volumetric gas adsorption technique using nitrogen, argon, etc. is a standard method for the determination of the surface areas and pore size/pore size distribution of finely divided porous samples [89]. The relation between the amount adsorbed and the equilibrium pressure of the gas at constant temperature is defined by the adsorption isotherm. The physisorption of gases such as N₂, O₂ and Ar has been studied to characterize the porosity [90-93]. The nitrogen adsorption isotherm for MCM-41 with pores of around 4.0 nm, which is type IV in the IUPAC classification [94], shows two distinct features: a sharp capillary

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condensation step at a relative pressure of 0.4 and no hysteresis between the adsorption and desorption branches (Fig. 2.10). The adsorption at very low relative pressure, $p/p_0$, is due to monolayer adsorption of $\text{N}_2$ on the walls of the mesopores and does not represent the presence of any micropores [95, 96]. The steep increase in $\text{N}_2$ adsorption (within the $p/p_0$ range between 0.2 to 0.4) corresponds to capillary condensation within uniform pores. The sharpness and the height of this step reflect the uniformity of the pore size and the pore volume respectively. However, in the case of materials with pores larger than 4.0 nm [97] or using $\text{O}_2$ or $\text{Ar}$ as adsorbate [91], the isotherm is still type IV but also exhibits well-defined hysteresis loops. The presence and size of the hysteresis loops depend on the adsorbate [91], pore size [97] and temperature [98].

The traditional method for analyzing pore-size distributions in the mesopore range is the Barrett–Joyner–Halenda (BJH) method [99, 100] which is based on the Kelvin equation and, thus, has a thermodynamic origin. However, compared with new methods that rely on more localized descriptions such as density functional theory (DFT) [96, 101] and Monte Carlo (MC) simulation [102], the thermodynamically based methods overestimate the relative pressure at desorption and therefore underestimate the calculated pore diameters by 1.0 nm. Moreover, the theoretical basis for the BJH analysis becomes fairly weak if the step at 77 K lies below $p/p_0=0.42$, because this is considered to be the stability limit of the meniscus. Pore sizes calculated in such cases are still probably in the right range, but a sound theoretical foundation for such values is missing.

**Fourier transform infrared spectroscopy (FTIR)** yields information concerning the structural details of a siliceous inorganic material [103, 104]. In addition, it can be used to confirm surface characteristics (such as acidity) and isomorphous substitution by other elements in the material. The technique allows to relate different materials by their common structural features, such as a classification of zeolite structures.

Broad bands in the region $\sim3400$ cm$^{-1}$ are assigned to $–\text{OH}$ stretching vibration of MCM-41 which could be associated to Si-OH and water vibrations, confirming the presence of the silanol groups [80, 105] or bridged hydroxyl
Chapter 2. Synthesis and Characterization of MCM-41 based materials

groups. Bands ~1650 cm\(^{-1}\) are attributed to H-O-H bending vibration. A broad band ~1300-1000 cm\(^{-1}\) is assigned Si-O-Si asymmetric stretching mode. Bands at 800 cm\(^{-1}\) and 458 cm\(^{-1}\) are attributed to symmetric stretching vibration and bending vibration (rocking mode) of Si-O-Si. The band at 960 cm\(^{-1}\) is assigned to the presence of Si-OH stretching vibration.

Fig. 2.8 X-ray diffraction pattern of high-quality calcined MCM-41 made by Huo and Margolese [46].

**Fig. 2.9** TEM of MCM-41 featuring 4.0 nm sized pores, hexagonally arranged [85].

**Fig. 2.10** Adsorption isotherm of nitrogen on MCM-41 with 4.0 nm pores at 77 K [91].

Thermal Analysis gives an idea about the thermal stability of the material and the possible phase changes that occur during the thermal treatment of the material. An understanding of the thermal behavior is of basic importance for utilizing the material in various temperature ranges where it is thermally stable.

Determining the quantity and strength of the acid sites is crucial to understanding and predicting the performance of a catalyst. Temperature-
**Chapter 2. Synthesis and Characterization of MCM-41 based materials**

**Programmed Desorption (TPD)** is one of the most widely used and flexible techniques for characterizing the acid sites on surfaces. Ammonia is a very basic molecule which is capable of titrating weak acid sites, which may not contribute to the activity of catalysts. The strongly polar adsorbed ammonia is also capable of adsorbing additional ammonia from the gas phase.

The acidity of different materials can be determined using the TPD of ammonia. This method involves three steps. The sample is first degassed and then saturated with a mixture of 5% NH$_3$+He gas at 120 °C, when ammonia gets chemisorbed on the acidic sites of the catalyst. After removal of any physisorbed ammonia from the surface by purging He at 120°C for 30 min, the temperature programmed desorption is carried out at a heating rate of 10 °C/min. The desorbed gas concentration is continuously monitored and recorded with temperature by a thermal conductivity detector (TCD). This concentration-temperature plot is referred to as the TPD profile. The area under the profile is proportional to the amount of gas desorbed. Acid sites with varying acid strength differ in their heat of adsorption, which is reflected in the TPD profile by way of a number of distinct peaks representing the acid sites of the catalyst. The acidity is reported as ml/g. The area under the curve indicates the amount of NH$_3$ desorbed and hence the number of surface acid sites. In general, amorphous materials exhibit broad desorption peaks compared to crystalline ones. Though the crystalline materials show sharper peaks indicating less number of acid sites, the desorption temperatures of NH$_3$ are high indicating strong acid sites. Since siliceous MCM-41 have a neutral framework, sharp desorption bands are absent in the NH$_3$-TPD profiles indicative of negligible surface acidity.

**Elemental analysis** gives us an idea about the composition of the catalyst. It is important to know the composition of a catalyst before use. Instrumental methods used for elemental analysis are Flame photometry, Atomic absorption spectroscopy (AAS) and Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) which are both popular as well as accurate. ICP-AES is a widely used analytical technique for the determination of elements present in a wide variety of samples. The technique is based on atomic emission spectroscopy, and as the name suggests, plasma is used as
Chapter 2. Synthesis and Characterization of MCM-41 based materials

the source of excitation/ionization of atoms. The intensity obtained for each sample is matched against a calibration plot prepared for the particular element for quantitative estimation. The concentration of different elements is actually measured at ppm level, which can be later converted into the % weight of the element, by incorporating the dilution factor. These values are then converted into moles of each element.

Energy dispersive X-ray analysis (EDX) is used for both identification of an element as well as to have a rough estimate of the composition of the materials. EDX is used in coordination with and as supportive analysis with ICP-AES which is more accurate compared to EDX.

Diffuse Reflectance UV-visible spectroscopy is a technique that measures the scattered light reflected from the surface of samples in the UV-visible range (200-800 nm). For most of the isomorphously substituted molecular sieves, transitions in the UV region (200-400) nm are of prime interest. This spectroscopic technique is used to determine the coordination state of transition metal ions substituted in the matrix of the molecular sieves, involving ligand-to-metal charge transfer transitions at ~ 200-220 nm.

Characterization of Al-MCM-41

Isomorphous substitution of a heteroatom in the framework of the molecular sieves results in changes in the unit cell parameters and unit cell volume. This is one of the ways to confirm isomorphous substitution. The XRD diffraction patterns for Al-MCM-41 are shown in Fig.2.11. The patterns illustrate the characteristics of a typical mesoporous MCM-41 structure. The \(d_{100}\) reflections of Al-MCM-41 have been shifted to higher values compared to its as-synthesized analogue. This is in agreement with Borade and Clearfield [106], suggesting the framework substitution of \(\text{Al}^{3+}\) in MCM-41 structure.

The FTIR spectrum of MCM-41 has already been discussed earlier in the text. It is observed that there is no significant change in the FTIR bands of Al-MCM-41 compared to silicon MCM-41. The band at 960 cm\(^{-1}\) is assigned to the presence of Si-OH stretching vibration as well as metal ion substituted MCM-41. A slight shift in band positions is observed due to isomorphous substitution of metal ion for Si\(^{4+}\).
For the $\text{Al}^{3+}$ incorporated MCM-41, sharp desorption bands are observed in the NH$_3$-TPD profiles indicating presence of surface acidity, combined with increase in surface acidity, with increase in $\text{Al}^{3+}$ content.

**Characterization of Heteropoly acid (HPA) supported MCM-41**

Heteropoly acid supported onto MCM-41 have been prepared and characterized exhaustively [80,105]. The three main reliable techniques used for characterization of these materials are XRD, FTIR and surface properties—pore size, pore size distribution, surface area and surface acidity which ensure the anchoring of HPA’s onto MCM-41, wherein comparisons are made between pure HPA’s, pure MCM-41 and a combination of these.

The XRD patterns of a typical mesoporous MCM-41 structure have been discussed earlier in the text, where importance of the $d_{100}$ reflection has been indicated. Fig.2.12 illustrates the effect of the HPA loading on the XRD of MCM-41 samples. HPA has a striking effect on the width and intensity of the main reflection at high $d_{100}$ spacing and this line becomes broader and weaker as the loading increases. This suggests that the long-range order of Si-MCM-41 is decreased noticeably by the presence of HPA. MCM-41 presents the highest surface area and pore volume, with all pores being in the mesopore range. The pore size distribution of MCM-41 shows a unique peak centered at about 25Å diameters as given in the literature [107]. With increasing HPA loading, a reduction in surface area, pore volume and a notable compression of the pore size distribution and increase in surface
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acidity are observed compared to MCM-41 (Table 2.2). Table 2.2 presents changes in textural properties with increase in HPA wt. %.

Table 2.2 Textural properties of various wt. % HPA loaded materials[105]

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>d_{100} (Å)</th>
<th>Unit cell a₀ (nm)</th>
<th>Surface area (m²/g)</th>
<th>Pore size BJH_ads (nm)</th>
<th>Pore volume BJH_ads (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-MCM-41</td>
<td>44.21</td>
<td>5.10</td>
<td>938</td>
<td>2.60</td>
<td>0.60</td>
</tr>
<tr>
<td>10wt.% 12-TPA-MCM-41</td>
<td>42.15</td>
<td>4.86</td>
<td>526</td>
<td>2.55</td>
<td>0.32</td>
</tr>
<tr>
<td>15wt.% 12-TPA-MCM-41</td>
<td>38.45</td>
<td>4.44</td>
<td>265</td>
<td>2.40</td>
<td>0.12</td>
</tr>
<tr>
<td>20wt.% 12-TPA-MCM-41</td>
<td>35.37</td>
<td>4.08</td>
<td>235</td>
<td>1.90</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Fig. 2.12 XRD pattern of the materials (a) Si-MCM-41, (b) 10wt.% 12-TPA-MCM-41, (c) 15wt.% 12-TPA-MCM-41, (d) 20wt.% 12-TPA-MCM-41 [80].

The FTIR spectra of HPA supported onto MCM-41 are given in Fig 2.13. A broad band due to –OH stretch of water in ~3400 cm⁻¹ region and the corresponding –OH₂ bending mode around ~1637 cm⁻¹ very well correlate with the water adsorption property (hydrophilic property) of the catalysts. Pure HPA spectra with a Keggin structure with four strong bands, at 1082 cm⁻¹ (P-O), 988 cm⁻¹ (W=O) and 800 cm⁻¹ (W-O-W), and a weak band at 525 cm⁻¹ (W-O-P) [108] are observed. The framework bands of Si-MCM-41 at 1236, 1090, 965, 800, 564 and 465 cm⁻¹ [109] easily overlap with those of HPA i.e. 12-tungsto phosphoric acid (12-TPA). For 10 wt.% 12-TPA-MCM-41, none of the 12-TPA bands are observed, except for a slight increase in the intensity of the
Chapter 2. Synthesis and Characterization of MCM-41 based materials

800 cm\(^{-1}\) band. For 15 wt.%12-TPA-MCM-41, the bands at 988 and 891 cm\(^{-1}\) become visible. With 20 wt.% of the 12-TPA loading, the 1082 cm\(^{-1}\) band become sharper and the intensity of the two bands at 988 and 891 cm\(^{-1}\) increases. Furthermore, it is observed that the intensity of 800 cm\(^{-1}\) band is almost proportional to the increase in the amount of 12-TPA. The final and most important evidence is the increase in surface acidity with increased 12-TPA loading.

2.10 EXPERIMENTAL

Materials: Commercial grade sodium silicate (Na\(_2\)SiO\(_3\)) with composition 28%SiO\(_2\) and 7.5% Na\(_2\)O was procured from Sapna Chemicals, Vadodara. CTABr, CPBr, sodium hydroxide flakes, aluminium sulfate, ammonium nitrate and 12-tungstophosphoric acid (12-TPA) were purchased from Loba Chemicals, Mumbai. Tetra ethylorth silicate (TEOS) and analytical grade sulphuric acid were obtained from E.Merck, Mumbai. All other chemicals and reagents used were of analytical grade. Double distilled water (DDW) was used for all studies.

Synthesis of MCM-41: In the present endeavor, the objective is to synthesize mesoporous MCM-41 at room temperature with good thermal stability and high surface area as well as retention of surface area at high temperature. A sol–gel method has been used to synthesize MCM-41 to achieve this objective. Several sets of materials were prepared varying conditions in each case, using surface area as an indicative tool in all cases. Table 2.3 describes the parameters that have been optimized for synthesis of MCM-41.

Synthesis of MCM-41 at optimized condition

As indicated in table-2.3 entry No.-8 indicates optimum condition. We hereby describe synthesis of MCM-41 under optimized conditions. The molar gel composition for MCM-41 is 1 SiO\(_2\):0.5 CTABr:0.25 Na\(_2\)O:80 H\(_2\)O. In a typical 500g batch size experiment, 63.02 g of Na\(_2\)SiO\(_3\) was mixed with 183 gDDW under continuous stirring at room temperature for ~15 min. in a polypropylene container (A). An aqueous solution of CTABr was prepared by dissolving 54.14 gm CTABr in 200 gm DDW under continuous stirring at room temperature (B). Template solution B was added to a precursor solution A dropwise with continuous stirring within ~15 min. and the solution further
Chapter 2. Synthesis and Characterization of MCM-41 based materials

stirred for 15 min. The pH of the resultant solution was adjusted to 10.5 using 1:1 H\textsubscript{2}SO\textsubscript{4}(diluted 1:1V/V). A gel was obtained at this stage which was stirred further for 30 min. The polypropylene container was now closed and allowed to age at room temperature without stirring for 24 h. The resultant gel was filtered, washed with DDW to remove adhering ions and dried at 120°C, followed by calcination at 550°C for 6 h at a heating rate of 2°C/min. The final material obtained was used for all further studies.

Note: In the present synthetic endeavor Na\textsubscript{2}SiO\textsubscript{3} as a silica source is preferred to TEOS, reasons being higher cost of TEOS. Further, the thermal stability of final material obtained is better when Na\textsubscript{2}SiO\textsubscript{3} is used as silica source compared to TEOS. While preparation it is preferable to add template to silica source. The pH of template being almost neutral and pH of silica being >12, if template is added to silica source, the pH variation window is narrowed down due to which pH of gel formation is easily adjusted. The pH in the synthesis was adjusted to 10.5 because gel viscosity is maximum at this pH, which can also be stirred with ease for homogenization. Finally at the optimized condition, surface area retention between 550 - 900 °C is fairly good.

Synthesis of Al-MCM-41

In the present synthetic endeavor the objective is to synthesize mesoporous Al-MCM-41 at room temperature with good thermal stability and high surface acidity. A sol-gel method has been used to achieve this objective. Several sets of materials were prepared varying silica to alumina ratios, apart from other conditions, where surface acidity has been used as an indicative tool in all cases. Table 2.4 describes parameters that have been optimized for synthesis of Al-MCM-41.

Synthesis of Al-MCM-41 at optimized condition

As indicated in optimization table 2.4 entry No-4 indicates optimum conditions. We hereby describe synthesis of Al-MCM-41 under optimized conditions. The molar gel composition of Al-MCM-41 is 1SiO\textsubscript{2}·0.033Al\textsubscript{2}O\textsubscript{3}·0.4CTABr·0.25Na\textsubscript{2}O·90H\textsubscript{2}O. In a typical 500g batch experiment, the first step was preparation of the precursor solution. 57.48 g of Na\textsubscript{2}SiO\textsubscript{3} was mixed with 197.5 g DDW under continuous stirring at room
Chapter 2. Synthesis and Characterization of MCM-41 based materials

temperature for ~15 min, in a polypropylene container, to which was added an aqueous solution of aluminium sulfate (prepared by dissolving 5.643 g aluminium sulfate in 40 g DDW) dropwise and with constant stirring within ~15 min. This is the precursor solution (A). An aqueous solution of CTABr was prepared by dissolving 39.5 g CTABr in 160 g DDW under continuous stirring at room temperature (B). Template solution (B) was added to precursor solution (A), dropwise and under constant stirring within ~15 min. The pH of the resultant solution was adjusted to ~10.5 using 1:1 H$_2$SO$_4$ (diluted 1:1V/V). A gel was formed which was further stirred for 30 min. The polypropylene container was now closed and allowed to age at room temperature without stirring for 24 hrs. The resultant gel was filtered, washed with DDW to remove adhering ions and dried at 120°C followed by calcination at 550°C for 6h, at a heating rate of 2°C/min. After thermal treatment, the samples with various Silica : Alumina ratios Al-MCM-41-20, Al-MCM-41-30, Al-MCM-41-50, and Al-MCM-41-100 were subjected to ion exchange by treating them with aqueous 1.0%NH$_4$NO$_3$ solution under continuous stirring for 3h, followed by calcination at 550°C for 3h at a heating rate of 2°C/min. in air flow. As indicated in Table 2.5 the sample Al-MCM-41-30 exhibits maximum surface acidity and was used for all further studies.

Note: In the present synthetic endeavor Na$_2$SiO$_3$ as a silica source is preferred to TEOS, reasons being higher cost of TEOS, thermal stability of final material obtained is better, and excess negative charge developed in the framework due to substitution of Si$^{4+}$ by Al$^{3+}$, requires Na$^+$ for charge balance. While preparation, it is preferable to add template to precursor source. The pH of template being almost neutral and pH of precursor being >12, if template is added to precursor source, the pH variation window is narrowed down due to which pH of gel formation is easily adjusted. The pH in the synthesis was adjusted to 10.5 because gel viscosity is maximum at this pH, which can also be stirred with ease for homogenization.

Further, lower the SiO$_2$:Al$_2$O$_3$ ratio, higher will be Al$^{3+}$ content and hence better is the acidity generated in the resulting materials. At the optimized condition surface acidity is high as well as surface area retention between 550 - 900 °C is fairly good.
### Chapter 2. Synthesis and Characterization of MCM-41 based materials

#### Table 2.3 MCM-41 Synthesis Strategies - Parameters optimized

<table>
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<tr>
<th>Parameters</th>
<th>No</th>
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<th>Template source</th>
<th>Template mole</th>
<th>H$_2$O mole</th>
<th>Temp. (°C)</th>
<th>Aging Time (h)</th>
<th>pH</th>
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*SiO$_2$ mole = 1 mole; RT = Room Temperature (30±3 °C); % SiO$_2$ = 99.89 (ICP-AES).*

#### Table 2.4 Al-MCM-41 Synthesis Strategies - Parameters optimized

<table>
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<tr>
<th>Parameters</th>
<th>No</th>
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<th>Al$_2$O$_3$ mole</th>
<th>SiO$_2$/Al$_2$O$_3$ Input mole ratio</th>
<th>Template mole</th>
<th>Element Analysis (ICP-AES)</th>
<th>SiO$_2$/Al$_2$O$_3$ Output mole ratio</th>
<th>*Total Acidity (ml/g)</th>
<th>BET Surface area at different Temperature (m$^2$/g)</th>
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<td>6.64</td>
<td>22.89</td>
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</tbody>
</table>

*SiO$_2$ Source = Na$_2$SiO$_3$; Al$_2$O$_3$ source = Al$_2$(SO$_4$)$_3$; Template Source = CTABr; H$_2$O mole = 90; RT = (30±3 °C); pH = 10.5; Aging Time = 24 h
*Details in Table 2.5.*
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Synthesis of 12-TPA supported MCM-41

The aim was to load different wt. % of 12-TPA onto MCM-41 and induce acidity into the material, using surface acidity as an indicative tool in all cases. Four samples of 12-TPA supported MCM-41 catalysts were prepared with varying 12-TPA loading (10-40 wt.%). In a typical setup (10% 12-TPA loading) 1g of 12-TPA was dissolved in 100 ml DDW, to which was added 9 g of MCM-41 synthesized as described earlier in the text, and the resultant slurry stirred continuously for 24h at room temperature. The excess solution was removed under vacuum, dried and subsequently calcined at 350 °C for 2h at a heating rate of 2°C/min. Table 2.6 shows that 20%12-TPA loaded sample exhibits maximum surface acidity and used for all studies.

2.11 MATERIAL CHARACTERIZATION

The synthesized materials in the present study MCM-41, Al-MCM-41 and 12-TPA supported onto MCM-41 were subjected to instrumental methods of analysis/characterization. Al-MCM-41 with SiO$_2$:Al$_2$O$_3$ = 30, abbreviated as Al-MCM-41-30 and 12-TPA supported onto MCM-41 with 12-TPA loading = 20 wt.%, abbreviated as 12TPA-MCM-41-20 have been used for characterization, as they exhibit highest surface acidity and used for all catalytic studies.

Instrumental Methods of Analysis

Elemental analysis was performed on ICP-AES spectrometer (Thermo Scientific iCAP 6000 series). X-ray diffractogram($2\theta$ = 1° - 40°) was obtained on X-ray diffractometer (Bruker D8 Focus) with Cu-K$_\alpha$ radiation with nickel filter. FTIR spectra was recorded using KBr pellet on Shimadzu (Model 8400S). Thermal analysis (TGA) was performed on a Shimadzu (Model TGA 50) thermal analyzer at a heating rate of 10 °C·min$^{-1}$. SEM and EDX of the sample were scanned on Jeol JSM-5610-SLV scanning electron microscope. TEM was performed using Philips CM30 ST electron microscope operated at 300kv. Surface area measurements were determined using Micromeritics Gemini at -196°C using nitrogen adsorption isotherms. Surface acidity was determined by NH$_3$-TPD method using Micromeritics Chemisorb 2720. UV-VIS.-diffuse reflectance spectra was obtained using Shimadzu(Model UV-DRS 2450).
**Chapter 2. Synthesis and Characterization of MCM-41 based materials**

**Characterization of MCM-41**

The XRD of MCM-41 is presented in (Fig. 2.14). A peak for $2\theta$ between $2^\circ$ and $3^\circ$ is observed which is characteristic of the Bragg plane reflection (100). This is evidence for MCM-41 structure [80,83,84,106].

A TEM image (Fig.2.15) shows hexagonal arrangement of uniform, ~3 nm sized pores indicative of MCM-41 structure. SEM (Fig.2.16) exhibits irregular morphology indicating amorphous nature of material. Elemental analysis performed by ICP-AES shows $\%$SiO$_2$ to be 99.89 (Table 2.3), which is also well supported by EDX (Fig.2.17) which shows atomic $\%$ of Si = 33.33 and atomic $\%$ of O = 66.67.

Surface areas ($A_{BET}$) determined by $N_2$ adsorption BET method, exhibits isotherms of type IV, in accordance with the IUPAC classification for mesoporous materials [94] (Fig.2.18 and Fig.2.19). Pore diameters (~3 nm) confirm the mesoporous nature of the synthesized materials with pore size distribution between 2-6 nm which are in the range usually observed for MCM-41 samples [110]. Surface area of MCM-41 calculated by BET method is 1136 m$^2$/g at 550 °C, 1121 m$^2$/g at 700 °C and 805 m$^2$/g at 900 °C.

The FTIR spectrum presented in Fig. 2.20 exhibits presence of broad bands in the region ~3400 cm$^{-1}$ assigned to –OH stretching vibration of MCM-41 which could be associated to Si-OH and water vibrations. Bands ~1630 cm$^{-1}$ are attributed to H-O-H bending vibration. A broad band ~1260-1000 cm$^{-1}$ is assigned Si-O-Si asymmetric stretching mode. Bands at 800 cm$^{-1}$ and 450 cm$^{-1}$ are attributed to symmetric stretching vibration and bending vibration (rocking mode) of Si-O-Si. The band at 960 cm$^{-1}$ is assigned to the presence of Si-O-H stretching vibration.

TGA thermogram (Fig. 2.21) exhibits an initial weight loss of ~10% in the temperature range 30-100 °C due to loss of moisture and hydrated water. Thereafter in the region 200-600°C there is a marginal/negligible weight loss which indicates fairly stable nature of the materials.

Absence of sharp desorption bands as well as negligible acidity in NH$_3$-TPD profiles (Fig.2.22) is indicative of a neutral MCM-41 framework.
Chapter 2. Synthesis and Characterization of MCM-41 based materials

Fig. 2.14 XRD of MCM-41

Fig. 2.15 TEM of MCM-41

Fig. 2.16 SEM of MCM-41

Fig. 2.17 EDX of MCM-41

Fig. 2.18 Nitrogen adsorption isotherm of MCM-41

Fig. 2.19 Pore distribution of MCM-41

<table>
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<tr>
<th>Element</th>
<th>Wt.%</th>
<th>At.%</th>
<th>Comp. %</th>
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</tr>
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<td>O</td>
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Chapter 2. Synthesis and Characterization of MCM-41 based materials

Characterization of Al-MCM-41-30

XRD of Al-MCM-41 is presented in Fig. 2.23. It is observed that there is shift in position of the peak characteristic of the Bragg plane reflection (100) for 2θ between 2° and 3° position indicating incorporation of $\text{Al}^{3+}$ in the framework of siliceous MCM-41. Further, with increase in $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio there is further shift in band position towards higher 2θ value.

TEM image of Al-MCM-41-30 (Fig.2.24) exhibits a well-defined hexagonal arrangement with a fairly uniform pore structure. SEM (Fig.2.25) of Al-MCM-41-30 exhibits irregular morphology. Elemental analysis performed by ICP-AES shows %$\text{SiO}_2$ and %$\text{Al}_2\text{O}_3$ to be 94.90 and 4.90 respectively(Table
Chapter 2. Synthesis and Characterization of MCM-41 based materials

2.4), which is also well supported by EDX (Fig.2.26) which shows atomic % of Al = 1.73, atomic % of Si = 31.89 and atomic % of O = 66.38.

Surface areas ($A_{BET}$) determined by N$_2$adsorption BET method exhibits isotherms of type IV, in accordance with the IUPAC classification for mesoporous materials [94] (Fig.2.27 and 2.28). Pore diameters (~3.5 nm) confirm the mesoporous nature of the synthesized material with pore size distribution between 2.2-5 nm which are in the range usually observed for Al-MCM-41 [110]. Surface area of Al-MCM-41-30 calculated by BET method is 580 m$^2$/g at 550°C, 510 m$^2$/g at 700°C and 470 m$^2$/g at 900°C (Table 2.3).

The FTIR spectrum presented in Fig. 2.29 exhibits wide bands in the region ~3400 cm$^{-1}$ assigned to –OH stretching vibration of MCM-41 which could be attributed to Si-OH and water vibrations. Bands ~1650 cm$^{-1}$ are attributed to H-O-H bending vibration. A broad band ~1260-1000 cm$^{-1}$ is assigned Si-O-Si asymmetric stretching mode. Bands at 795 cm$^{-1}$ and 450 cm$^{-1}$ are attributed to symmetric stretching vibration and bending vibration (rocking mode) of Si-O-Si. The band at 960 cm$^{-1}$ is assigned to the presence of Si-O-Al stretching vibration.

TGA thermogram (Fig. 2.30) exhibits an initial weight loss of ~20% in the temperature range 30-100 °C due to loss of moisture and hydrated water. Thereafter in the region 200-600°C there is a marginal/negligible weight loss which indicates fairly stable nature of the material.

NH$_3$-TPD patterns of Al-MCM-41 with varying SiO$_2$:Al$_2$O$_3$ ratios are presented in Fig.2.31. Al-MCM-41-30 exhibits highest surface acidity (table-2.5). Surface acidity of samples is presented in Table 2.5.

Fig. 2.32 presents UV-VIS-DRS of Al-MCM-41 with varying SiO$_2$:Al$_2$O$_3$ ratio. Rise in intensity of band ~ 210 nm region is observed with increasing Al$^{3+}$ incorporation. The incorporation of Al$^{3+}$ in the silica framework is further evident from surface acidity values and elemental analysis results (Table 2.5).
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Fig. 2.23 XRD of Al-MCM-41-30

Fig. 2.24 TEM of Al-MCM-41-30

Fig. 2.25 SEM of Al-MCM-41-30

Fig. 2.26 EDX of Al-MCM-41-30

Element | Wt. % | At. % | Comp. %
--- | --- | --- | ---
Al | 2.33 | 1.73 | 4.41
Si | 44.69 | 31.89 | 95.59
O | 52.98 | 66.38 |
Totals | 100 |
Formula: SiO$_2$ and Al$_2$O$_3$

Fig. 2.27 Nitrogen adsorption isotherm of Al-MCM-41-30

Fig. 2.28 Pore distribution of Al-MCM-41-30
Chapter 2. Synthesis and Characterization of MCM-41 based materials

Characterization of 12-TPA-MCM-41

FTIR spectra of HPA supported onto MCM-41 have been detailed earlier in the text. The FTIR spectra (Fig. 2.33) with different 12-TPA loading coincide well with those observed in literature [105,106,108]. The surface acidity increases gradually with increasing 12-TPA loading from 10 to 20 wt.%, after which a decrease is observed (Table 2.6).

SEM image of 12TPA-MCM-41-20 (Fig. 2.34) exhibits irregular morphology. EDX of 12TPA-MCM-41-20, presented in Fig.2.35 shows the presence of W as atomic % = 2.20, Si atomic % = 30.44 and O atomic % = 67.40. Absence of P in EDX is probably due very low % of P in the original compound, which is probably not detected in EDX due to instrument limitations.
Chapter 2. Synthesis and Characterization of MCM-41 based materials

Fig. 2.33 FT-IR of 12-TPA-MCM-41

Element | Wt.% | At.% | Comp. %
---|---|---|---
W | 17.30 | 2.20 | 21.81
Si | 36.55 | 30.44 | 78.19
O | 46.15 | 67.40 |
Totals | 100 |
Formula | SiO$_2$ and WO$_3$

Fig. 2.34 SEM of 12-TPA-MCM-41-20

Fig. 2.35 EDX of 12-TPA-MCM-41-20

Fig. 2.36 Ammonia TPD of 12-TPA-MCM-41

Fig. 2.37 XRD of 12-TPA-MCM-41

A=MCM 41, b=10% TPA-MCM-41 c=20%, d=30%, e=40% , f=12-TPA
Chapter 2. Synthesis and Characterization of MCM-41 based materials

Comparative TPD pattern of MCM 41 samples with different 12-TPA loading (Fig.2.36) exhibits two distinct peaks at 200°C and 600°C indicating presence of medium and strong acid sites respectively in all the samples. Surface acidity of samples is presented in Table 2.6.

XRD of different wt% loading of 12-TPA-MCM-41 are presented in Fig. 2.37. With reference to MCM-41 (a) and 12-TPA (f) b, c, d, e shows that 12-TPA is loaded onto MCM-41. e with the highest loading shows that the 12-TPA remains on the surface and the X-ray pattern is close towards (f). The observed results coincide well with those observed in literature [105,106].

<table>
<thead>
<tr>
<th>Table 2.5. Surface acidity of Al-MCM-41 with various SiO$_2$:Al$_2$O$_3$ ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td>Materials</td>
</tr>
<tr>
<td></td>
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<tr>
<td></td>
</tr>
<tr>
<td>Al-MCM-41-20</td>
</tr>
<tr>
<td>Al-MCM-41-30</td>
</tr>
<tr>
<td>Al-MCM-41-50</td>
</tr>
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<td>Al-MCM-41-100</td>
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<table>
<thead>
<tr>
<th>Table 2.6. Surface acidity of different wt.% 12TPA loaded onto MCM-41</th>
</tr>
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<tbody>
<tr>
<td>Materials</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Siliceous MCM-41</td>
</tr>
<tr>
<td>10% 12-TPA-MCM-41</td>
</tr>
<tr>
<td>20% 12-TPA-MCM-41</td>
</tr>
<tr>
<td>30% 12-TPA-MCM-41</td>
</tr>
<tr>
<td>40% 12-TPA-MCM-41</td>
</tr>
</tbody>
</table>

2.12 APPLICATION OF Al-MCM-41 AND 12-TPA-MCM-41 AS SOLID ACID CATALYSTS

In chapter I, the importance of Green Chemistry, 12 principles of Green Chemistry, and how Green Chemistry goals can be achieved through catalysis has been discussed in details. Further, solid acid catalyst as an
alternative approach to liquid acid catalyst and its advantages over liquid acid catalyst and important materials used as solid acid catalysts for various organic transformations has been discussed. Siliceous MCM-41 has poor/negligible catalytic activity due to framework neutrality, however with high thermal stability and surface area. Thus, the aim of the present work was to induce catalytic properties into MCM-41 and encash the advantageous properties such as thermal stability and surface area, and put the resulting material to practical use. The answers to these questions are emergence of inherent acidity in Al-MCM-41 and induced acidity in 12TPA-MCM-41. Theory, synthesis and characterization of these materials are well described in the preceding pages in the text of this chapter (Section 2.10 and 2.11). In the present study the utility of Al-MCM-41 and 12TPA-MCM-41 as solid acid catalysts using Esterification and Friedel-Crafts alkylation and acylation as model reactions has been explored.

2.13 ESTERIFICATION

Esterification is a widely employed reaction in the organic process industry. Esters fall under a very wide category, ranging from aliphatic to aromatic with various substitutions and multifunctional groups, organic esters being valuable intermediates in the chemical industry. Esters are mostly used as plasticizers, solvents, perfumery and flavour chemicals, and also as precursors to many pharmaceuticals, agrochemicals and fine chemicals.

Esters are carboxylic acid derivatives with the general formula R-COOR' (R,R'=H, alkyl or aryl). When a carboxylic acid is treated with a large excess of an alcohol, in presence of an acid catalyst, an ester is formed. The reaction is called acid catalyzed esterification or sometimes Fischer esterification after the great German chemist Emil Fischer. The esterification process introduced by E.Fischer and A. Speier (1895) consists in refluxing acid and excess methanol or ethanol in presence of about 3% hydrogen chloride. The reaction is represented as follows.

\[
\text{RCOOH} + \text{R'OH} \xrightleftharpoons{H^+} \text{RCOOR'} + \text{H}_2\text{O} \tag{2.3}
\]

The conventional esterification is an equilibrium reaction. For the stoichiometric mixture of acid and alcohol, equilibrium generally reaches
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~68% [111] of conversion for the straight chain saturated alcohol. In order to obtain maximum yields Le Chatlier’s principle, is followed and the reaction is driven to the right hand side/forward direction, as follows:

**Addition of one of the reactants in excess:** The reaction usually reaches a point of equilibrium at ~60% conversion, but in a small scale experiment a conversion of 60-80% can be achieved by use of a large excess of either acid or alcohol.

**Removal of one of the products:** Either ester or water formed is removed as soon as it is formed. Generally, suitable organic solvents are employed to remove the water formed during the reaction as a binary azeotrope or by employment of dehydrating agent such as anhydrous magnesium sulfate or molecular sieves [112].

**Synthetic routes to monoesters and diesters**

 Monoesters are typically synthesized by [113,114] (1) Solvolytic reactions (2) Condensation reactions (3) Free radical processes (4) Miscellaneous processes. The synthesis of mono esters can be presented as shown in equation 2.1.

 Diesters are prepared in two stages (Scheme 2.2) [115] e.g. reaction between phthalic anhydride with alcohol. The first stage is very rapid and can be carried out in the absence of a catalyst. However, esterification of the second carboxylic group is very slow and needs to be facilitated by an acid catalyst, resulting in the formation of water as a byproduct. The reaction is an equilibrium one and hence to facilitate it in the forward direction, the water molecule must be removed by azeotrope formation. The current commercial process is a batch method which is very efficient with respect to its feed stocks. Conversion (based on phthalic anhydride) and selectivity can reach 99.2 and 99.8 %, respectively. To reach this high conversion, a 20 % excess of alcohol is used. The excess is recovered after reaction by a steam stripping process. Hardly any purification is required after synthesis because of the high selectivity, usually only a decolorization is carried out. A typical byproduct is the dialkyl ether formed by the condensation of two molecules of alcohol.
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First step

\[
\text{Phthalic anhydride} + \text{ROH} \xrightarrow{\text{Heat}} \text{Monoester}
\]

\[R = 2\text{-ethyl hexanol}\]

Second step

\[
\text{Monoester} + \text{ROH} \xrightarrow{\text{Heat, Solvent, Solid acid}} \text{Diester} + \text{H}_2\text{O}
\]

Scheme 2.2 Schematic presentation of diester formation

Problems / limitations in esterification

For the preparation of perfumery and flavour grade esters, only a few of the above mentioned routes can be considered, due to the stringent specifications of the final product. Normally, liquid phase catalysts such as sulphuric acid, p-toluene sulfonic acid, methanesulfonic acid, hydrochloric acid, phosphoric acid etc. have been used, that are cited as potential environmentally hazardous chemicals that pose problems such as difficulty in handling, causing acidic waste water, difficulty of catalyst recovery etc. [116,117]. These catalysts are known to colour the product and cannot be reused. As already mentioned, these liquid acids have several disadvantages. Due to these problems, accompanied by the increasing environmental awareness, there is a global effort to replace the conventional liquid acids by suitable solid acids. The most widely employed and supposedly cleaner production technique for such esters, involves the reaction of the appropriate carboxylic acid with an alcohol using a heterogeneous catalyst such as solid acid catalyst under reflux conditions, followed by separation of the ester by distillation.
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2.14 LITERATURE SURVEY IN THE CURRENT AREA OF STUDY

Monoesters using various solid acid catalysts

Cation exchange resins Dowex 50W and Amberlite IR-120 [118,119] have been used as solid acid catalysts in the esterification of acetic acid with isobutanol. Esterification of acrylic and lactic acids with butanol using Amberlyst-15 [120, 121] and lactic and salicylic acids with methanol using Dowex 50W resin as solid acid catalysts [122,123] has been reported. Salmi et al [124] have studied methyl acetate formation on new polyolefin supported sulfonic acid catalysts. Meunier has reported esterification reactions using Nafion as solid acid catalyst [125]. Kaolinite [126] as well as montmorillonite [127] clay has been used as catalyst in the esterification of carboxylic acids. Giovanni Sartori has written an excellent review on clay catalyst for monoesterification reaction [128]. Manohar et al [129] have reported esterification of acetic acid and benzoic acid using ZrO$_2$ and Mo-ZrO$_2$ as solid acid catalysts and found that Mo-ZrO$_2$ exhibits better catalytic activity than ZrO$_2$. Vishwanathan et al. [130] have reported esterification by solid acid catalysts including clays, zeolites, sulphated metal oxides and heteropolyacids. Toor et al. [131] have reported kinetic study of esterification of acetic acid with n-butanol and isobutanol catalyzed by ion exchange resin. Silicotungstic acid supported zirconia is reported as an effective catalyst for esterification reactions using formic, acetic, propionic, n-butyricacid and n-butyl alcohol, isobutyl alcohol and sec-butyl alcohol [132]. Chu et al [133] have reported the vapour phase synthesis of ethyl and butyl acetate by immobilized dodecatungstosilicic acid on activated carbon. The rate of esterification was found to be dependent on the partial pressure of the reactants. Dupont et al [134] have reported heteropolyacids supported on activated carbon as catalysts for the esterification of acrylic acid by butanol. Deactivation of the catalyst was observed under flow conditions (from 43 to 32% conversion) and was due to the dissolution of the supported HPA in the reaction medium (25 %). Timofeeva et al [135] have reported esterification of acetic acid and n-butyl alcohol using Keggin and Dawson type HPAs and found that the reaction rate depends on the acidity, as well as on the structure.
and composition of HPAs. The Dawson type heteropoly acids exhibited higher activity compared to the Keggin type HPAs. In the esterification reaction of acetic acid and n-butyl alcohol, the catalytic activity of HPAs has a good correlation with the dissociation constant of HPAs. 12-TPA supported on hydrous zirconia was used as solid acid catalyst in esterification of primary and secondary alcohols [136]. Sharath et al studied benzyl acetate formation in the presence of zeolites and their ion exchanged forms. They reported reasonably good yield with 100 % selectivity [137]. Ma et al have reported the synthesis of ethyl, butyl and benzyl acetates with high yields using zeolitecatalyst [138]. From our laboratory, TMA salts have been widely investigated as solid acid catalysts for synthesis of monoesters such as ethyl acetate (EA), propyl acetate (PA), butyl acetate (BA) and benzyl acetate (BzA) [139-146].

**Diestersusing various solid acid catalysts**

Suter has reported a noncatalytic process for the manufacture of DOP, at very high temperatures, at which autocatalysis occurs [147]. Bekkum and Schwegler investigated the use of HPAs (homogeneous and carbon supported) for DOP synthesis [148]. They obtained a superior activity at low temperatures in both homogeneous and supported form. Yadav et al [149] have reported the use of solid super acids (sulfated and HPA supported onto oxides) for the synthesis of DOP. They have reported a selectivity > 99 % and demonstrated that selection of optimum calcination temperature is a must for the optimum yield. Yadav et al[150] also have reported esterification of maleic acid with ethanol over cation-exchange resin catalysts. G Lu [151] also investigated DOP synthesis over solid superacids $\text{SO}_4^{2-}/\text{Ti-M-O}$ ($\text{M} = \text{Al, Fe, Sn}$). They obtained superior activity in case of $\text{SO}_4^{2-}/\text{Ti-Al-Sn-O}$ system and found that acid strength, surface area and catalytic activity of the system is affected by the preparation conditions. Ma et al [152] studied the synthesis of DOP using ZSM-5 and HY zeolites. Z H Zhao [153] has also reported the use of aluminophosphate and silicoaluminophosphate molecular sieves as solid acid catalyst for the synthesis of DOP. Amini et al [115] have reported the use of heteropoly acids for the production of DOP and DBP. DEM synthesis has been reported by Reddy et al [154] using montmorillonite clay, but the yield is
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low (41%) and relatively high amount of catalyst (0.5 g) was used. In another report, DEM was synthesized by Jiang et al [155] using the reaction of CO with ClCH₂COOC₂H₅. In this case high yield was observed but the reaction was carried out at high pressure. Kolah et al [156] have reported esterification of succinic acid with ethanol and also have reported esterification of tri-ethyl citrate via mono and di-ethyl citrate catalyzed by macroporous Amberlyst-15 ion exchange resin. From our laboratory, TMA salts have been widely investigated as solid acid catalysts for synthesis of diesters such as dioctyl phthalate (DOP), dibutyl phthalate (DBP) and diethyl malonate (DEM) [144-146,157].

Monoesters and diesters using MCM-41 type materials

Jiang et al [158] have studied catalytic activity of mesoporous TiO₂ solid super acid for esterification of iso-amyl alcohol and salicylic acid. Salmi et al [159] have studied methyl acetate formation on polyolefin supported sulfonic acid catalysts. Sugi et al [160] have reported 12-TPA supported onto MCM-48 as an efficient catalyst for the esterification of long chain fatty acid and alcohols in supercritical CO₂. Yarmo et al [161] have reported 12-TPA supported on MCM-41 for esterification of fatty acid under solvent free condition. The workers have also reported synthesis, characterization and catalytic performance of porous nafion resin/silica nanocomposites for esterification of lauric acid and methanol [162]. Nascimento et al [163] have reported catalytic esterification of oleic acid over SO₄²⁻/MCM-41 nanostructured materials. Helen et al [164] have reported use of mesoporous silica supported diarylammonium catalysts for esterification of free fatty acid in greases. Zhu et al [165] have reported synthesis, characterization and application of sulfated zirconia/hexagonal mesoporous silica (HMS) catalyst in the esterification of gossypol. Pandurangan et al. [166] have reported vapour phase esterification of butyric acid with 1-pentanol and tert-butylbenzene with iso-propyl acetate over Al-MCM-41 mesoporous molecular sieves. Srinivas et al. [167] have reported the kinetics of esterification of fatty acids over solid acid catalysts including large pore zeolite-β (Hβ), micro-mesoporous Fe/Zn double-metal cyanide (DMC) and mesoporous Al-MCM-41. Said et al [168] have reported perspective catalytic performance of Brønsted acid sites during
Chapter 2. Synthesis and Characterization of MCM-41 based materials

esterification of acetic acid with ethyl alcohol over 12-TPA supported on silica. Rhijn et al[169] have reported sulfonic acid functionalized ordered mesoporous materials as catalysts for condensation and esterification reactions. Zhang Yijun et al. [170] have reported synthesis, characterization and catalytic application of HPA/MCM-48 in the esterification of methacrylic acid with n-butyl alcohol. Lingaiah et al. [171] have reported 12-TPA with varying contents on SnO₂ as efficient solid acid catalysts for esterification of free acids with methanol for the production of biodiesel. Valdeilson et al [172] have studied esterification of acetic acid with alcohols using supported niobium pentoxide on silica-alumina catalysts. These catalysts were found to be highly stable and active in esterification reaction. Patel et al [173] have reported synthesis and characterization of 12-TPA anchored to MCM-41 as well as its use as environmentally benign catalyst for synthesis of succinate and malonate Diesters.

Conclusions

As mentioned in the above quoted literature, esterification reactions have been widely investigated using several solid acids such as sulfated metal oxides, zeolites, ion exchange resins, HPA, metal oxides, pillared clays etc. Though solid acid catalysts are emerging as alternatives to liquid acid catalysts a literature survey reveals that there are several limitations e.g. though sulfated metal oxide is a very good esterification catalyst, it gets easily deactivated by losing the sulfate ions, thereby recycling of the catalyst is restricted. In case of HPA, the separation is difficult and when supported on carbon the activity decreases. Sulfonic acid based resin (Nafion-H) has also been found to be unsatisfactory due to its low operating temperature. Hence, new materials are continuously being synthesized and explored as solid acid catalysts to overcome the above mentioned limitations. Thus, the endeavour – “Global effort to replace conventional liquid acid catalysts by solid acid catalysts” is on.

As already indicated earlier in the text siliceous MCM-41 has a poor/negligible catalytic activity due to framework neutrality. Catalytic properties have been induced into siliceous MCM-41 via incorporation of Al³⁺ into the MCM-41 lattice to result in a catalyst with inherent acidity. HPAs have
proved to be the alternative for traditional acid catalysts due to both strong
cidity and appropriate redox properties. The major disadvantage of HPAs, as
catalyst lies in their low thermal stability, low surface area (1-10 m$^2$/g) and
separation problems from reaction mixture due to its high solubility in polar
solvent. HPAs can be made eco-friendly, insoluble solid acids, with high
thermal stability and high surface area by supporting them onto suitable
supports. The support provides an opportunity for HPAs to be dispersed over
a large surface area which increases catalytic activity. Thus, catalytic
properties have been induced into MCM-41 by supporting a HPA onto MCM-
41 by process of anchoring and calcination to result in a catalyst with induced
acidity.

In the present endeavour 12TPA-MCM-41(Induced Acidity) and Al-
MCM-41(Inherent Acidity) have been used as solid acid catalysts using
esterification as a model reaction wherein monoesters such as Ethyl Acetate
(EA), Propyl acetate (PA), Butyl acetate (BA) and Benzyl acetate (BzA) and
diesters such as Diocetyl phthalate (DOP), Dibutyl phthalate (DBP) and Diethyl
malonate(DEM) have been synthesized. The catalytic activity of 12TPA-MCM-
41 and Al-MCM-41 have been compared and correlated with surface
properties of the materials.

2.15 EXPERIMENTAL

Materials: Acetic acid, ethanol, 1-propanol, 1-butanol, benzyl alcohol,
cyclohexane, toluene, xylene, phthalic anhydride, 2-ethyl 1-hexanol, malonic
acid were procured from Merck.

Catalyst Synthesis: The synthesis and characterization of 12-TPA-MCM-41
(with various wt.% of 12-TPA loading) and Al-MCM-41 (with varying SiO$_2$:Al$_2$O$_3$
ratios) have been discussed earlier in the text (Section 2.10 and 2.11). It is
observed that 12-TPA-MCM-41 with 20wt.% 12-TPA loading abbreviated as
12TPA-MCM-41-20 and Al-MCM-41 with SiO$_2$:Al$_2$O$_3$ ratio 30 abbreviated as
Al-MCM-41-30 exhibit highest surface acidity and thus used for all catalytic
studies.

Synthesis of monoesters (EA, PA, BA and BzA): In a typical reaction, a 100
mL round bottomed flask equipped with a Dean and Stark apparatus,
attached to a reflux condenser was used and charged with acetic acid (0.05 –
0.10 M), alcohol (0.05 - 0.10 M), catalyst (0.10 - 0.20 g) and a suitable solvent (15 mL). Cyclohexane was used as a solvent for the synthesis of ethyl acetate and toluene for propyl acetate, butyl acetate and benzyl acetate. The reactions were carried out varying several parameters such as amount of catalyst, mole ratio of reactants, reaction time and these parameters optimized. After completion of reaction, catalyst was separated by decantation and reaction mixture was distilled to obtain the product.

**Synthesis of diesters (DEM, DOP and DBP):** The diesters were synthesized in two steps. In the first step, equimolar proportion (0.025 mole) of acid and alcohol (malonic acid and ethanol for DEM, phthalic anhydride and 2-ethyl 1-hexanol for DOP, phthalic anhydride and 1-butanol for DBP) were taken in a round bottomed flask and the reaction mixture stirred at ~80 °C for DEM, ~145 °C for DOP, and ~115 °C for DBP for about 10-15 min in absence of any catalyst and solvent. The dicarboxylic acid and anhydride are completely converted to the monoester, so that the acid concentration at this stage is taken as the initial concentration. The obtained product (monoester) was then subjected to esterification reaction by addition of a second mole (0.025 mole) of respective alcohol, catalyst (0.10 - 0.20 g) and 15 mL solvent (toluene for DEM and DBP and xylene for DOP). The reactions were carried out varying several parameters such as amount of catalyst, mole ratio of reactants, reaction time and these parameters optimized. In all cases the round bottomed flask was fitted with Dean and Stark apparatus, with a condenser to remove water formed during the reaction. After completion of reaction, catalyst was separated by decantation and reaction mixture was distilled to obtain the product.

**Regeneration and recyclability of catalyst:** During the course of the reaction, many a time the catalyst colour changes. This is probably due to the adsorption of reacting molecules coming onto the surface of the catalyst. After separation of catalyst in reaction mixture by decantation, it is first refluxed in ethanol for 30 minutes, followed by drying at 120°C. This material was used as recycled catalyst. This regeneration procedure was followed in subsequent recycle reaction.
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Calculation of % yield of esters: For both mono and diesters, % yields were determined by titrating the reaction mixture with 0.1 M alcoholic KOH solution. The yields of the esters were calculated using the formula, % yield = [(A - B) / A] × M × 100, where A and B are acid values of the sample withdrawn before and after reaction and M is mole ratio of acid: alcohol. The yield of ester formed was also determined using GC.

2.16 RESULTS AND DISCUSSION

Monoesterification

Equilibrium constants of the esterification reactions are low. As in any equilibrium reaction, the reaction may be driven to the product side by controlling the concentration of one of the reactants (Le Chatlier’s Principle). When concentration of one of the reactant relative to the other is increased, the reaction is driven to the product side. In order to obtain higher yield of esters, Le Chatlier’s Principle has been followed. Solvents cyclohexane and toluene have been employed to remove the water formed during the reaction as a binary azeotrope. Monoesters EA, PA, BA and BzA were synthesized as described in experimental section.

Firstly, reaction conditions were optimized using 12TPA-MCM-41-20 as solid acid catalyst for BzA synthesis by varying such parameters as catalyst amount, initial mole ratio of the reactant (alcohol to acid) and reaction time, and the results obtained presented in Table 2.7 and a graphical presentation (Fig. 2.38 and 2.39).

During optimization of reaction time, it is observed that the conversion rate was very high initially, indicating that the reaction obeys first order kinetics. As reaction time increases, percentage yield increases. However, there is not much gain in product after 8 h. Hence, the optimum reaction time was selected as 8 h. With increasing amount of the catalyst, the % yield increased which is due to proportional increase in the number of active sites. The influence of reactant ratio (alcohol: acid) was studied by increasing from 1:1.5 to 1.5:1. The yield can be increased by increasing the concentration of either alcohol or acid. As observed from Table 2.7, the % yield of ester increases with increase in mole ratio of acid while decreases with increasing mole ratio of alcohol. This may be attributed to preferential adsorption of
alcohol on the catalyst which results in blocking of active sites. For economic reasons also, the reactant that is usually less expensive of the two is taken in excess. In the present study, acids were used in excess. The temperature parameter has not been varied, due to the fact that the reaction temperature is sensitive to boiling points of reactants as well as solvents used as azeotrope.

At the optimum condition (mole ratio of reactants, alcohol:acid = 1:1.5, amount of catalyst = 0.15 g, time = 8 h) mono esters EA, PA and BA have been synthesized and the yields of esters are presented in Table 2.8. Further, for comparative study, Al-MCM-41-30 is used as solid acid catalyst for synthesis of mono esters BzA, EA, PA and BA at the above mentioned optimum condition. The results are presented in Table 2.8.

It is observed that, the order of % yield of ester formed for both catalysts is BzA > EA > PA > BA. Though the yields in case of mono esters using both catalysts are comparable, higher yields are observed in case of 12TPA-MCM-41-20 which could be attributed to higher surface acidity. Turn over number (TON) reflects the effectiveness of a catalyst and this also follows the order of ester formation.

Esterification of monoesters EA, PA and BA has been reported [153] in absence of catalyst and exhibit poor yields. Therefore catalyst is a must for these reactions. In case of BzA however, it is observed that with an excess of acetic acid and in the absence of any catalyst the yield is as high as 90.6 % which is attributed to auto catalysis. In another report [137] high yields of BzA were obtained with small amount of the catalyst but the reaction time was relatively high. In the present study, yields of BzA are ~95% for both catalysts compared to above literature reports. Higher yields in case of benzyl acetate could be attributed to an enhanced nucleophilicity due to presence of aromatic ring in benzyl alcohol. The order of % yield of ester formed is EA > PA > BA could be explained due to increase in carbon chain length in the respective alcohols used for ester formation. During condensation of these alcohols with acetic acid probably steric effects are responsible for explaining decreasing yields from EA through PA to BA.
% yields obtained in recycled catalyst and % decrease in yields in subsequent cycles is presented in Table 2.8 and 2.9 respectively, and a graphical presentation (Fig. 2.40). It is observed that in subsequent cycles decrease in % yields is less for Al-MCM-41-30 compared to 12TPA-MCM-41-20. This could probably be due to the leaching of 12-TPA from surface of MCM-41. It is observed that the colour of the catalyst changes after each catalytic run. This gives an indication that during the course of the reaction the reacting molecules come onto the surface of the catalyst. Some of them enter into reaction to give the product while a few of them get adsorbed on the surface, which is marked by the change in the colour of the catalyst. The fact that the reactant molecules are weakly adsorbed is evident from the catalyst regaining its original colour, when treated with ethanol. The possibility of molecules entering interstices cannot be ruled out. This is observed from the fact that the yields go down after every regeneration, leading to deactivation of the catalyst.

---

**Fig.2.38** Reaction time variation for BzA synthesis

**Fig.2.39** Catalyst amount variation for BzA synthesis

**Fig.2.40** Comparative catalyst performance in the formation of monoesters
## Chapter 2. Synthesis and Characterization of MCM-41 based materials

Table 2.7 *Optimization of reaction conditions for monoesters using 12-TPA-MCM-41-20.*

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Reactants with their mole ratio</th>
<th>Product</th>
<th>Catalyst amount (g)</th>
<th>Time (h)</th>
<th>Temp. (°C)</th>
<th>%Yield 12-TPA-MCM-41-20</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) Time variation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Bz + AA (1:1)</td>
<td>BzA</td>
<td>0.1</td>
<td>1</td>
<td>115</td>
<td>31.54</td>
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<tr>
<td>3</td>
<td>Bz + AA (1:1)</td>
<td>BzA</td>
<td>0.1</td>
<td>2</td>
<td>115</td>
<td>46.43</td>
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<td>BzA</td>
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<td>3</td>
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<td>Bz + AA (1:1)</td>
<td>BzA</td>
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<td>4</td>
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<td>BzA</td>
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<td>5</td>
<td>115</td>
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<td>BzA</td>
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<td>6</td>
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<td>(B) Catalyst amount optimization</td>
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<td>11</td>
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</tr>
<tr>
<td>(C) Mole ratio optimization</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td><strong>Bz + AA (1:1.5)</strong></td>
<td>BzA</td>
<td><strong>0.15</strong></td>
<td>8</td>
<td>115</td>
<td><strong>95.23</strong></td>
</tr>
<tr>
<td>14</td>
<td>Bz + AA (1.5:1)</td>
<td>BzA</td>
<td>0.15</td>
<td>8</td>
<td>115</td>
<td>62.50</td>
</tr>
</tbody>
</table>

*Bz = Benzyl alcohol; AA = Acetic acid; Entry No.13 is optimum condition.*
Chapter 2. Synthesis and Characterization of MCM-41 based materials

Table 2.8 % yields of monoesters using 12-TPA-MCM-41-20 and Al-MCM-41-30 at optimized condition

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Reactants</th>
<th>Product</th>
<th>12TPA-MCM-41-20</th>
<th>Al-MCM-41-30</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>%Yield *TON</td>
<td>%Yield *TON</td>
</tr>
<tr>
<td>1</td>
<td>Bz + AA</td>
<td>BzA</td>
<td>95.23 34.12</td>
<td>93.55 34.50</td>
</tr>
<tr>
<td>2</td>
<td>E + AA</td>
<td>EA</td>
<td>92.31 33.10</td>
<td>90.35 33.10</td>
</tr>
<tr>
<td>3</td>
<td>P + AA</td>
<td>PA</td>
<td>90.23 33.00</td>
<td>88.25 33.56</td>
</tr>
<tr>
<td></td>
<td>B + AA</td>
<td>BA</td>
<td>74.13 18.50</td>
<td>73.16 17.59</td>
</tr>
</tbody>
</table>

A Reusability of catalyst

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Reactants</th>
<th>Product</th>
<th>12TPA-MCM-41-20</th>
<th>Al-MCM-41-30</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Bz + AA 1st cycle</td>
<td>BzA</td>
<td>87.15 31.35</td>
<td>89.73 31.70</td>
</tr>
<tr>
<td>5</td>
<td>Bz + AA 2nd cycle</td>
<td>BzA</td>
<td>77.45 20.82</td>
<td>83.80 27.80</td>
</tr>
<tr>
<td>6</td>
<td>E + AA 1st cycle</td>
<td>EA</td>
<td>87.10 31.89</td>
<td>85.20 29.20</td>
</tr>
<tr>
<td>7</td>
<td>E + AA 2nd cycle</td>
<td>EA</td>
<td>78.65 21.40</td>
<td>79.15 22.00</td>
</tr>
<tr>
<td>8</td>
<td>P + AA 1st cycle</td>
<td>PA</td>
<td>84.42 28.51</td>
<td>85.41 29.15</td>
</tr>
<tr>
<td>9</td>
<td>P + AA 2nd cycle</td>
<td>PA</td>
<td>78.35 21.14</td>
<td>80.25 23.00</td>
</tr>
<tr>
<td>10</td>
<td>B + AA 1st cycle</td>
<td>BA</td>
<td>69.00 17.50</td>
<td>69.45 15.45</td>
</tr>
<tr>
<td>11</td>
<td>Bz + AA 1st cycle</td>
<td>BA</td>
<td>61.48 12.00</td>
<td>64.32 14.55</td>
</tr>
</tbody>
</table>

Bz = Benzyl alcohol; AA = Acetic acid; E = Ethanol; P = 1-Propanol; B = 1-Butanol; Mole ration of the reactants = 1.5:1 (Acid:Alcohol); Reaction Time = 8 h. Catalyst amount = 0.15 g; Reaction temperature 80°C for EA and 115°C for PA, BA and BzA; *TON = Turn over number, gram of ester formed per gram of catalyst.

Table 2.9% Decrease in yields of monoesters using regenerated catalysts in subsequent cycles

<table>
<thead>
<tr>
<th>Monoesters</th>
<th>12TPA-MCM-41-20</th>
<th>Al-MCM-41-30</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1st Cycle</td>
<td>2nd Cycle</td>
</tr>
<tr>
<td>BzA</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>EA</td>
<td>5</td>
<td>9</td>
</tr>
<tr>
<td>PA</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>BA</td>
<td>4</td>
<td>8</td>
</tr>
</tbody>
</table>
Chapter 2. Synthesis and Characterization of MCM-41 based materials

Diesterification

Diesters DEM, DOP and DBP were synthesized as described in experimental section.

Firstly, reaction condition was optimized using 12TPA-MCM-41-20 as solid acid catalyst for DEM synthesis by varying such parameters as catalyst amount, reaction time, temperature and mole ratio of the acid and alcohol. The results obtained are presented in Table 2.10 and a graphical presentation 2.42 and 2.43.

Diesters are prepared in two stages (Scheme 2.2). The first stage is very rapid and can be carried out in the absence of a catalyst. In second stage with increasing amount of the catalyst, the % yield increases which is due to proportional increase in the number of active sites. In diester formation the acid/anhydride taken as substrate possesses two attacking sites responsible for ester formation. Thus, only concentration of alcohol was varied following Le Chatlier’s Principle in the present study. The influence of reactant ratio (alcohol: acid) was studied increasing from 2:1 to 2.4:1. It is observed that the % yield of diester was maximum with 2:1 mole ratio. As reaction time increases, percentage yield increases. However, there is not much gain in product after 8 h. Hence, the optimum reaction time was selected as 8 h.

At optimum condition (mole ratio of reactants, alcohol: diacid/anhydride = 2: 1, amount of catalyst = 0.15 g, time = 8 h) diesters DOP and DBP have been synthesized. Results are presented in Table 2.11. Further, for comparative study, at optimized condition Al-MCM-41-30 is used as solid acid catalyst for synthesis of diesters DEM, DOP and DBP. The results are presented in Table 2.11.

From Table 2.11, it is observed that, there is no marginal difference in the yields of DOP and DBP and order of the % yields of diesters formation is DEM > DOP ≈ DBP, which is probably due to less steric hindrance felt by incoming ethanol from monoethyl malonate formed in the first step in case of DEM.

The mechanism of diester formation over solid acid catalyst is similar to that of conventional mechanism involving the formation of protonated dicarboxylic acid, using proton donated by the catalyst, followed by
Chapter 2. Synthesis and Characterization of MCM-41 based materials

nucleophilic attack of alcoholic group to yield the respective monoester. The second carboxylic group present in monoester gets further esterified by the same mechanism in a repeat reaction, which ultimately results in the diester formation [154].

Fig. 2.41 Reaction time variation for DEM synthesis

Fig. 2.42 Catalyst amount variation for DEM synthesis

Fig. 2.43 Comparative catalyst performance in the formation of diesters

% yields obtained in recycled catalyst and % decrease in yields in subsequent cycles is presented in Table 2.11 and 2.12 respectively, and a graphical presentation (Fig. 2.43). It is observed that in subsequent cycles decrease in % yields is less for Al-MCM-41-30 compared to 12TPA-MCM-41-20. This is could probably be due to leaching of 12-TPA from surface of catalyst. The change in colour of catalyst is also observed after each catalytic run. The same explanation can be forwarded as discussed in case of monoester formation.
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Table 2.10 Optimization of reaction conditions for DEM using 12TPA-MCM-41-20.

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Reactants with their mole ratio</th>
<th>Product</th>
<th>Catalyst amount (g)</th>
<th>Time (h)</th>
<th>Temp. (°C)</th>
<th>%Yield 12-TPA-MCM-41-20</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Time variation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>E + MA (2:1)</td>
<td>DEM</td>
<td>0.1</td>
<td>2</td>
<td>115</td>
<td>16.66</td>
</tr>
<tr>
<td>2</td>
<td>E + MA (2:1)</td>
<td>DEM</td>
<td>0.1</td>
<td>4</td>
<td>115</td>
<td>41.66</td>
</tr>
<tr>
<td>3</td>
<td>E + MA (2:1)</td>
<td>DEM</td>
<td>0.1</td>
<td>6</td>
<td>115</td>
<td>50.01</td>
</tr>
<tr>
<td>4</td>
<td>E + MA (2:1)</td>
<td>DEM</td>
<td>0.1</td>
<td>8</td>
<td>115</td>
<td>53.33</td>
</tr>
<tr>
<td>B</td>
<td>Catalyst amount variation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>E + MA (2:1)</td>
<td>DEM</td>
<td>0.05</td>
<td>8</td>
<td>115</td>
<td>44.21</td>
</tr>
<tr>
<td>6</td>
<td>E + MA (2:1)</td>
<td>DEM</td>
<td>0.15</td>
<td>8</td>
<td>115</td>
<td>53.79</td>
</tr>
<tr>
<td>C</td>
<td>Mole ratio variation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>E + MA (2.2:1)</td>
<td>DEM</td>
<td>0.15</td>
<td>8</td>
<td>115</td>
<td>44.44</td>
</tr>
<tr>
<td>8</td>
<td>E + MA (2.4:1)</td>
<td>DEM</td>
<td>0.15</td>
<td>8</td>
<td>115</td>
<td>46.45</td>
</tr>
</tbody>
</table>

E = Ethanol, MA = Malonic Acid; Entry No. 6 is optimum condition.

Table 2.11 % yield of diesters using 12TPA-MCM-41-20 and Al-MCM-41-30 at optimized condition

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Reactants</th>
<th>Product</th>
<th>12TPA-MCM-41-20</th>
<th>%Yield</th>
<th>*TON</th>
<th>Al-MCM-41-30</th>
<th>%Yield</th>
<th>*TON</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>E + MA</td>
<td>DEM</td>
<td>53.79</td>
<td>20.18</td>
<td>18.80</td>
<td>48.40</td>
<td>45.10</td>
<td>18.08</td>
</tr>
<tr>
<td>2</td>
<td>PA + O</td>
<td>DOP</td>
<td>53.36</td>
<td>19.89</td>
<td>19.00</td>
<td>42.32</td>
<td>40.82</td>
<td>16.25</td>
</tr>
<tr>
<td>3</td>
<td>PA + B</td>
<td>DBP</td>
<td>52.92</td>
<td>19.00</td>
<td>19.00</td>
<td>43.05</td>
<td>40.38</td>
<td>14.00</td>
</tr>
<tr>
<td>A</td>
<td>Reusability of catalyst</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>E + MA1st cycle</td>
<td>DEM</td>
<td>48.41</td>
<td>18.80</td>
<td>18.08</td>
<td>45.10</td>
<td>18.08</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>E + MA2nd cycle</td>
<td>DEM</td>
<td>42.01</td>
<td>14.41</td>
<td>13.75</td>
<td>35.54</td>
<td>13.75</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>PA + O1st cycle</td>
<td>DOP</td>
<td>50.12</td>
<td>19.25</td>
<td>14.15</td>
<td>40.82</td>
<td>40.82</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>PA + O2nd cycle</td>
<td>DOP</td>
<td>44.70</td>
<td>16.00</td>
<td>14.20</td>
<td>36.2</td>
<td>36.2</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>PA + B 1st cycle</td>
<td>DBP</td>
<td>49.36</td>
<td>19.00</td>
<td>14.00</td>
<td>40.38</td>
<td>40.38</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>PA + B 2nd cycle</td>
<td>DBP</td>
<td>44.00</td>
<td>15.86</td>
<td>12.60</td>
<td>34.58</td>
<td>34.58</td>
<td></td>
</tr>
</tbody>
</table>

PA = Phthalic anhydride; O = 2-ethyl-1-hexanol; B = 1-Butanol; E = Ethanol; MA = Malonic Acid; Mole ration of the reactants = 1:2 (Acid/Anhydride:Alcohol); Reaction Time = 8 h. Catalyst amount = 0.15 g; Reaction temperature 115°C for DOP and 145°C DEM and DOP; *TON = Turn over number, gram of ester formed per gram of catalyst.
Table 2.12% Decrease in yields of diesters using regenerated catalysts in subsequent cycles

<table>
<thead>
<tr>
<th>Monoesters</th>
<th>12TPA-MCM-41-20</th>
<th>Al-MCM-41-30</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% Decrease in yields</td>
<td>% Decrease in yields</td>
</tr>
<tr>
<td></td>
<td>1&lt;sup&gt;st&lt;/sup&gt; Cycle</td>
<td>2&lt;sup&gt;nd&lt;/sup&gt; Cycle</td>
</tr>
<tr>
<td>DEM</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>DOP</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>DBP</td>
<td>8</td>
<td>5</td>
</tr>
</tbody>
</table>

Conclusions
The work outlined herein reveals the promising use of 12TPA-MCM-41-20 and Al-MCM-41-30 as solid acid catalysts in the synthesis of monoesters and diesters, the advantages being operational simplicity, mild reaction conditions and eco-friendly nature of catalyst. The monoesters and diesters formed can be simply distilled over, there is no catalyst contamination in products formed, no acid waste formation and products are colourless a limitation in the conventional process. The catalysts can be regenerated and reused. Since the reactions are driven by surface acidity of the catalyst, there is scope of obtaining better/higher yield by synthesizing material with high surface acidity by modifying synthesis procedure. Though yields of monoesters are high, the diester yields are low however, with the only advantage of the product having no colour contamination.

2.17 FRIEDEL-CRAFTS ACYLATION AND ALKYLATION
Charles Friedel and James Crafts in 1877 developed a set of reactions popularly known today as Friedel-Crafts reactions, involving electrophilic aromatic substitution of two types, acylation and alkylation.

Friedel-Crafts acylation
Friedel-Crafts acylation (Scheme 2.3) involves the reaction of an acyl chloride or acid anhydride with aromatic compounds in presence of a strong Lewis acid catalyst. Due to the electron-withdrawing effect of the carbonyl group, the ketone product is always less reactive than the original molecule, therefore multiple acylations do not occur, which is an advantage over the alkylation reaction (described later in the text). Also, there are no
carbocation rearrangements, as the carbonium ion is stabilized by a resonance structure in which the positive charge is on the oxygen, inhibiting intra molecular reactions.

Scheme 2.3 Reaction scheme for Friedel Crafts acylation

Mechanism for Friedel Crafts Acylation:
As seen from Scheme 2.4, the first step consists of dissociation of a chlorine atom to form an acyl cation. This is followed by nucleophilic attack of the arene towards the acyl group. Finally, a chlorine atom reacts to form HCl, and the AlCl₃ catalyst is regenerated:

Scheme 2.4 Reaction mechanism for Friedel Crafts acylation

The viability of the Friedel-Crafts acylation depends on the stability of the acyl chloride reagent. For example, in synthesis of benzaldehyde via the Friedel-Crafts pathway using formyl chloride as an acylating agent, since formyl chloride is too unstable to be isolated, formyl chloride has to be
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synthesized in situ. This is accomplished via the Gattermann-Koch reaction, accomplished by reacting benzene with carbon monoxide and hydrogen chloride under high pressure, catalyzed by a mixture of aluminium chloride and cuprous chloride.

Friedel–Crafts acylation of aromatic compounds and aromatic heterocyclic compounds is a ubiquitous reaction in the production of aromatic ketones, largely used as intermediates in the synthesis of pharmaceuticals, naproxen, dextromethorphan, ibuprofen and dyes, fragrances, and agrochemicals [174-179]. In particular, the synthesis of substituted acetophenones employing acylation is an important step for the production of a variety of precursors which find application in the production of pharmaceuticals, paint additives, photo initiators, fragrances, plasticizers, dyes and other commercial products [180-184].

Friedel-Crafts alkylation

Friedel-Crafts alkylation (Scheme 2.5) involves the alkylation of an aromatic ring and an alkyl halide using a strong Lewis acid catalyst. With anhydrous aluminium chloride as a catalyst, the alkyl group substitutes the chloride ion.

\[
\text{Scheme 2.5 Reaction scheme for Friedel Crafts alkylation}
\]

Mechanism for Friedel Crafts Alkylation

\[
R-\text{Cl} + \text{AlCl}_3 \rightarrow R^+ + \text{AlCl}_4^-
\]

\[
\text{Scheme 2.6 Reaction mechanism for Friedel Crafts alkylation}
\]
As seen from Scheme 2.6, the first step consists of dissociation of a chlorine atom to form an alkyl cation. This is followed by nucleophilic attack of the arene towards the alkyl group. Finally, a chlorine atom reacts to form HCl, and the AlCl$_3$ catalyst is regenerated.

In this reaction, the product is more nucleophilic than the reactant due to the electron donating effect of alkyl-chain, therefore, another hydrogen is substituted with an alkyl-chain, which leads to overalkylation of the molecule. Further, if the chlorine is not on a tertiary carbon, carbocation rearrangement reaction occurs, attributed to the relative stability of the tertiary carbocation over the secondary and primary carbocations. Steric hindrance can be exploited to limit the number of alkylations, as in the tertiary butylation of 1,4-dimethoxybenzene (Scheme 2.7)

Scheme 2.7 Reaction scheme for t-butylation of 1,4-dimethoxybenzene.

Scheme 2.8 Reaction scheme for Friedel Crafts alkylation using bromonium ion as electrophile

Alkylations are not limited to alkyl halides. Friedel-Crafts alkylation is possible with any carbocationic intermediate such as those derived from alkenes and a protic acid or lewis acid, enones and epoxides. In one study, the electrophile is a bromonium ion derived from an alkene and N-
bromosuccinimide (NBS). In this reaction samarium(III) triflate is believed to activate the NBS halogen donor in halonium ion formation (Scheme 2.8).

The liquid phase benzylation of benzene and other aromatic compounds by benzyl chloride is important for the production of diphenylmethane and substituted diphenylmethanes which are industrially important compounds used as pharmaceutical intermediates and fine chemicals [185-189].

The use of acyl halides or anhydrides as acetylation agents and soluble Lewis acids as catalysts is polluting, expensive and difficult to work with. In normal practice, strong mineral acids, such as H$_2$SO$_4$, HF, or supported Lewis-acid catalysts like anhydrous AlCl$_3$/SiO$_2$ and BF$_3$/SiO$_2$ are used for such reactions. However, these Lewis acids are consumed in more than stoichiometric amounts due to the formation of 1:1 molar adduct with aromatic ketones and further, the subsequent separation of the product by hydrolysis is cumbersome and generates a large amount of environmentally hazardous and corrosive waste.

Friedel-Crafts alkylation reactions catalyzed by homogeneous Lewis acid catalysts generally give complex reaction mixtures. The formation of reactant (and product) catalyst complexes, the increased tendency of alkylated products towards further alkylation and isomerization, coupled with the long contact of the reactant with the catalyst, result in decreased product selectivity.

As indicated earlier in the text owing to stringent and growing environmental regulations worldwide, there is a global effort to replace the conventional liquid acid catalysts by solid acids, which are less toxic, easily regenerable from the product, easy to handle and reuseable. In this context, the focus has been towards design of processes to replace homogeneous Lewis acid catalysts with environmentally benign heterogeneous catalysts. The acid sites in solid acids being milder than the conventional Lewis acids, would also inhibit side reactions such as polyalkylation, isomerization, transalkylation, dealkylation and polymerization that occur in traditional procedure. There is, therefore, substantial interest to carry out alkylation reactions with solid acid catalysts which decrease these side reactions.
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2.18 LITERATURE SURVEY IN THE CURRENT AREA OF STUDY

Acylation/alkylation of aromatic compounds have been reported using several solid acid catalysts in recent years. Kantam et al [189] have reported Friedel–Crafts acylation of aromatics and heteroaromatics using microcrystalline β zeolites with different acid anhydrides. The micronized β-zeolite shows manifold activity over normal zeolite in acylation reactions of aromatics. Deutsch et al [190] have reported acylation and benzylation of various aromatics on sulfated zirconia and observed that the rate of acylation reactions is dependent on the nature of the respective aromatic compound. The application of sulfated zirconia as a catalyst for the acetylation of aromatics was only successful in case of anisole amongst various aromatic compounds used. Kaur et al [191] have reported Friedel–Crafts acylation of anisole and toluene with acetic anhydride using HPA supported on silica as catalyst as well as H-β Zeolite. In contrast to anisole, the acylation of toluene with HPA is far less efficient than that with H-β. The inhibited activity of HPA for toluene could be attributed to preferential adsorption of acetic anhydride on the catalyst. Beers et al [192] have reported use of dealuminated β–zeolites as solid acid catalyst for acylation of anisole with octanoic acid and proposed a structure–activity relation for the same. After dealumination, increased activity and selectivity were found in the acylation of anisole with octanoic acid. The enhanced activity is suggested to result from higher accessibility of the active sites associated with framework-connected aluminum atoms. Bachiller-Baeza et al [193] have studied and compared the behaviours of HPA catalysts supported on a commercial silica and on a silica–zirconia mixed oxide for the acylation of anisole with acetic anhydride. The yields of p-methoxyacetophenone were highest for HPA/SiO₂. Castro et al [194] have reported a mechanistic overview on the acylation reactions of anisole using α,β unsaturated organic acids as acylating agents and solid acids as catalysts. The mechanism of acylation of anisole with α,β unsaturated acids, i.e. acrylic, crotonic and methylcrotonic acid, have been investigated using 12-PTA, supported on SiO₂ and in the form of cesium salts as catalysts. Since
α,β unsaturated acid can either alkylate and/or acylate the aromatic compound, the influence of the catalyst on the selectivity for these two competing reactions was studied. Analysis of products obtained on the acylation of aromatic compounds with α,β unsaturated acids shows that all the catalysts are more active for acylation than alkylation. Secondary products coming from intermolecular reactions of the acylated product with anisole as well as tertiary products coming from its further decomposition and recombination with another anisole molecule were observed. Heteropolyacids supported on silica were found to be more active and selective towards acylation reactions than zeolites HY and Hβ. Melero et al [195] have reported Friedel Crafts acylation of aromatic compounds over arenesulfonic acid containing mesostructured SBA-15 materials. Arenesulfonic acid centers anchored on the pore surface of a mesostructured SBA-15 material show greater activity (normalised to the concentration of sulfonic groups) as compared to other homogeneous and heterogeneous sulfonated catalysts and even in solventless conditions. This high activity is accompanied with a remarkable thermal stability of the acid centers, without leaching of sulfur species during the reaction.

Cardoso et al [196] have reported silica supported HPA catalyst for acylation of anisole using acetic anhydride as acylating agent. High conversions and very high p-selectivity were attained in the temperature range of 61–110 °C. However, deactivation was observed due to strong adsorption of the products. Ma et al [197] have reported Friedel-Crafts acylation of anisole over Y-zeolite catalyst with alkanolic acids, anhydrides and substituted benzoic acids. When carboxylic acids were used as acylating agents, the activity of the Y zeolite increased with its Lewis acidity, showing that the Lewis acid sites were more active than the Bronsted acid sites. Further, the reaction mechanism was found to be similar to the homogeneous catalysis, that is, the electrophilic intermediate formed from the acylating agent over zeolite acid sites attacked the aromatic ring of anisole. Gaare et al [198] have reported effect of lanthanum ion exchange and Si/Al ratio of Y-zeolite on the Friedel-Crafts acylation of anisole by acetyl chloride and acetic anhydride. For the rare-earth modified zeolites, the activity was
found to be dependent on the lanthanum content, and the yield increased with the level of lanthanum, even up to 93% exchange. Dealuminated Y-zeolites were also found to be very active, and an almost linear increase in the yield with decreasing aluminium fraction was found attributed to the increased hydrophobicity of dealuminated zeolites. Heidekum et al [199] have reported use of Nafion/Silica composite materials as solid acid catalysts for acylation reactions and claimed that entrapping nanosized Nafion particles in a silica-matrix, effectively enhances the accessibility of the acid sites in comparison to the original material, Nafion resin. Chaudhari et al [200] have reported AlCl₃-grafted Si-MCM-41 prepared by reacting anhydrous AlCl₃ with terminal Si–OH groups as an active and a reusable (if not exposed to atmosphere) mesoporous solid catalyst for the Friedel–Crafts benzylation and acylation reactions. However, like anhydrous AlCl₃, it is highly moisture sensitive and loses its activity on exposure to moist atmosphere. The active species on the catalyst are (–Si-O)ₙAlCl₃₋ₙ (n = 1–3). Cseri et al [201] have reported alkylation of benzene and toluene with benzyl chloride and benzyl alcohol over a series of clays obtained by exchanging the original cations of K10 by Ti⁴⁺, Fe³⁺, Zr⁴⁺, Cu²⁺, Zn²⁺, Ce³⁺, Cr³⁺ and Sn²⁺ cations. The acidity of these solids has been determined by infra red spectrometry using pyridine as molecular probe. The acidity of K10 clays can be changed to a great extent by cation exchange and by the thermal treatments applied to the solids. The rate of alkylation is roughly related to acidity when the substrate is benzyl alcohol, but not when benzyl chloride is used. In that case, the catalysts containing reducible cations (Fe³⁺, Sn⁴⁺, Cu²⁺) exhibit high activities in spite of their low number of acid sites. Bachari et al [202-204] have investigated benzylation of benzene and substituted benzenes, employing benzyl chloride as the alkylation agent over mesoporous silica with different Sn, Cu and Ga contents. The mechanism involves a redox step at the reaction initiation. The large pores of the mesoporous catalyst donot limit the size of the molecules that could be reacted. Chaudhary et al [205] have investigated benzylation of benzene by benzyl chloride to diphenyl methane over InCl₃, GaCl₃, FeCl₃ and ZnCl₂ supported on commercial clays (viz. Montmorillonite-K10, Montmorillonite-KSF and Kaolin) or on high silica mesoporous MCM-41. The redox function
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created due to the impregnation of the clays or Si-MCM-41 by InCl₃, GaCl₃, FeCl₃ or ZnCl₂ seems to play a very important role in the benzylation process. Kinetics of the benzene benzylations (using excess of benzene) over the supported metal chloride catalysts has also been investigated and a plausible reaction mechanism for the benzylations over the supported metal chloride catalysts is proposed. Silva et al [206] have evaluated catalytic activity of gel and macrotreticular ion-exchange resins (Lewatit and Amberlyst-15) for the reaction of benzene with benzyl alcohol and benzyl chloride at 80°C in the liquid phase. With benzylchloride, the monobenzylation product, diphenylmethane, was obtained in low yield, both with the gel and the macrotreticular resins. Better results were obtained with benzyl alcohol as benzylating agent and the most active resin was Amberlyst-15, the conversion of benzyl alcohol being proportional to the concentration of acid sites on the resin. Mantri et al [207] have investigated Friedel–Crafts alkylation of aromatics with benzyl alcohol as alkylation agent over rare earth metal triflates, Sc(OTf)₃, Hf(OTf)₄, La(OTf)₃, and Yb(OTf)₃ supported on MCM-41. The catalytic activity of triflates, was enhanced after being loaded onto MCM-41 due to increased dispersion, and gave the benzylated product in high yield. The rate of the benzylations of benzene was accelerated by electron donating groups and retarded by electron withdrawing groups. Narender et al [208] have studied benzylations of benzene and toluene with benzyl alcohol over a series of zeolites and metal modified β zeolites. A reaction mechanism has been proposed for formation of diphenylmethane and benzyl ether. Benzyl ether formation from benzyl alcohol is explained on the basis of the intermolecular reaction pathway, involving Bronsted acidsites of the zeolite. Bachari et al [209] have reported benzylations of benzene by benzyl chloride to diphenylmethane over FeCl₃, InCl₃, GaCl₃, ZnCl₂, CuCl₂ and NiCl₂ supported on mesoporous SBA-15. Further it is claimed that the redox property due to the impregnation of the SBA-15 by transition metal chloride, seems to play a very important role in the benzene benzylations process. Zhou et al [210] have reported silica-supported polytrifluoromethanesulfosiloxane (SiO₂–Si–SCF₃) catalyzed Friedel–Crafts benzylations of benzene and substituted benzenes. It was found that SiO₂–Si–SCF₃ could catalyze Friedel–
Crafts benzylation of benzene and substituted benzenes with benzyl alcohol under relatively mild experimental conditions. Reactions are very clean and water is the only by-product of the reaction. The yields amounted to 97–100%. Vinu et al [211] have reported benzylation of benzene and other aromatics by benzyl chloride over mesoporous Al-SBA-15 catalysts. Okuhara et al [212] have explained various HPAs, like H₃[PW₁₂O₄₀] and H₄[SiW₁₂O₄₀], were used as solid acid catalysts for the alkylation of 1,3,5-trimethylbenzene with γ-butyrolactone to form 4-(2,4,6-trimethylphenyl) butyric acid. The catalysts could be reused. Sugi et al [213] have reported Friedel–Crafts benzylation of aromatics with benzyl alcohols catalyzed by heteropoly acids such as 12-TPA (H₃PW₁₂O₄₀·xH₂O)(HPW), molybdophosphoric acid (H₃PMo₁₂O₄₀·xH₂O) (HPMo) and tungstosilicic acid (H₄SiW₁₂O₄₀·xH₂O) (HSiW) supported on mesoporous silica such as MCM-41, FSM-16 and SBA-15 by the impregnation method to enhance the catalytic activity of these solid acids by their dispersion on the support with high surface area. They also have used rare earth metal triflates supported on MCM-41 mesoporous silica. Donghao et al [214] have successfully prepared mesoporous silica materials, SBA-15, functionalized with strong (-SO₃H), moderate (-PO₃H₂) and weak (-COOH) acid groups and these mesoporous acid catalysts have been applied to the alkylation of phenol with tert-butanol. Subramaniam et al [215] have reported synthesis and characterization of HPA catalysts and their cesium salts, catalysts have been evaluated for the alkylation of isobutane with 1-butene. Angelis et al [216] have reported solid acid catalysts based on HPAs supported on different oxides catalyze the alkylation of isobutane with n-butenes to yield high-octane gasoline components. Ramos-Galvan et al [217] have reported alkylation of benzene with propylene over 12-TPA supported on MCM-41 and -48 type mesoporous materials. Chaudhari et al [218] have reported highly active Si-MCM-41 supported Ga₂O₃ and In₂O₃ catalysts for Friedel-Crafts-type benzylation and acylation reactions in presence or absence of moisture. Mohammad et al [219] have reported benzylation of benzene over sulfated zirconia supported as MCM-41 using a single source precursor. Kalabasi et al. have reported vapor phase alkylation of toluene using various alcohols over H₃PO₄/MCM-41 catalyst: influence of
reaction parameters on selectivity and conversion. Selvaraj et al [220] have reported synthesis of 2-acetyl-6-methoxynaphthalene using mesoporous \( \text{SO}_4^{2-} / \text{Al-MCM}-41 \) molecular sieves. Murugesan et al [221] have reported synthesis, characterization and catalytic activity of \( \text{Al-MCM}-41 \), \( \text{Fe,Al-MCM}-41 \) and \( \text{Zn,Al-MCM}-41 \) in the vapor phase alkylation and acylation of ethylbenzene with ethyl acetate in the temperature range between 250 and 400 °C. Endud et al [222] have reported cubic aluminated mesoporous materials, \( \text{Al-MCM}-48 \) as highly effective catalysts for Friedel-Crafts acylation of 2-methoxynaphthalene and 2-acetyl-6-methoxynaphthalene. Iwamoto et al [223] have reported Friedel-Crafts acylation of anisole with carboxylic anhydrides of large molecular sizes on mesoporous silica \( \text{MCM}-41 \) catalyst. Halligudi et al [224] have reported 12-TPA supported over zirconia in mesoporous channels of \( \text{MCM}-41 \) as catalyst in veratrole acetylation. Liquid-phase Friedel–Crafts alkylation and acylation reactions have been reported using aluminosilicate \( \text{MCM}-41 \) [225-229].

Conclusions

As mentioned in the above quoted literature, Friedel-Crafts acylation and alkylation reactions have been widely investigated using various solid acids, however with several limitations such as, Friedel-Crafts acylation and alkylation was successful only with certain substrates [191], leaching in case of supported catalysts, generation of secondary products [194], catalyst deactivation when exposed to moisture [200] etc. Many of the reactions using solid acid catalysts were also not economically viable. Such catalysts must be designed that are both economically viable and able to withstand industrial conditions. Thus, our endeavour as mentioned earlier in the text— “Global effort to replace conventional liquid acid catalysts by solid acid catalysts” is on. In continuation we herein report the catalytic activity of 12TPA-\( \text{MCM}-41\)-20 (Induced Acidity) and \( \text{Al-MCM}-41\)-30 (Inherent Acidity) as solid acid catalysts using Friedel-Crafts acylation and alkylation as model reactions wherein 4-methoxy acetophenone (4MA), 3,4-dimethoxy acetophenone (3,4DMA) and p-benzyl toluene (PBT) have been synthesized under solvent free conditions. The activity of both catalysts have been compared and correlated with surface properties of the materials.
2.19 EXPERIMENTAL

Materials: Anisole, acetic anhydride, veratrole, benzyl chloride and toluene were procured from Merck India.

Catalyst Synthesis: The synthesis and characterization of 12-TPA-MCM-41 (with various wt.% of 12-TPA loading) and Al-MCM-41 (with varying SiO$_2$:Al$_2$O$_3$ ratios) have been discussed earlier in the text (Section 2.10 and 2.11). It is observed that 12-TPA-MCM-41 with 20wt.% 12-TPA loading abbreviated as 12TPA-MCM-41-20 and Al-MCM-41 with SiO$_2$:Al$_2$O$_3$ ratio 30, abbreviated as Al-MCM-41-30 exhibit highest surface acidity and thus used for all catalytic studies.

Experimental setup for Friedel-Crafts acylation and alkylation: The reactions were carried out in a two necked 50 ml round bottomed flask equipped with a magnetic stirrer under heating in an oil bath. In a typical set up, a mixture of anisole or veratrole (10 mmol) and acetic anhydride (15 mmol) for acylation and toluene (10 mmol) and benzyl chloride (15 mmol) for alkylation, along with the catalyst (0.2 g) were taken in a round bottomed flask and stirred at 110°C for three hours. In all the reactions the substrates were used as solvents and hence the reaction temperature was kept according to solvent used (reflux temperature) for all the studies. The reactions were monitored by GC. After completion of reaction, the catalyst was separated by decantation, and reaction mixture was distilled to obtain the products 4 MA, 3,4DMA and PBT, the boiling points being ~273°C, 286°C and 300°C respectively.

Regeneration and recyclability of catalyst: During the course of the reaction, many a time the catalyst colour changes. This is probably due to the adsorption of reacting molecules coming onto the surface of the catalyst. After separation of catalyst in reaction mixture by decantation, it is first refluxed in ethanol for 30 minutes, followed by drying at 120°C. This material was used as recycled catalyst. This regeneration procedure was followed in subsequent recycle reaction.
2.20 RESULTS AND DISCUSSION

Firstly, reaction condition was optimized using 12TPA-MCM-41-20 as solid acid catalyst for 3,4DMA synthesis by varying such parameters as catalyst amount, initial mole ratio of the reactants, reaction time and temperature. The results obtained have been presented in Table 2.13 and a graphical presentation (Fig. 2.44 to 2.47).

Friedel crafts acylation of veratrole with acetic anhydride, gave selectively 3,4 DMA. It is observed that yield increases with reaction time until equilibrium is reached within 4 h. For the same reaction time, yield increases with increasing catalyst amount, since the number of active sites per gm of substrate increases. The influence of reactant ratio (veratrole:acetic anhydride) was studied increasing from 1:0.75 to 1:2. It is observed that the % yield of 3,4DMA was maximum with 1:1.5 mole ratio. (Table 2.13)

It has been reported earlier that there is no significant effect of solvents in the acylation of anisole and veratrole and best results were obtained when aromatic ethers were used as self solvents [189]. In the present study therefore anisole and veratrole (aromatic ethers) have been used both as substrates and solvent and for this reason while optimizing reaction condition, concentration of only the acylating agent was varied. Thus, the Green Chemistry principle 5 which states that the “use of solvents should be made unnecessary whenever possible and when used, innocuous” is implemented. Further, the boiling point of solvent was taken as reaction temperature. However, when reaction temperature is varied (100 °C and 120 °C), there is no significant change in % yield. Therefore 70°C is optimized as reaction temperature for 3,4DMA synthesis.

At optimum condition (mole ratio of reactants, veratrole:acetic anhydride = 1: 1.5, amount of catalyst = 0.2 g, time = 4 h) 4MA and PBT have been synthesized. Acylation of anisole with acetic anhydride gave selectively 4-methoxy acetophenone (4 MA) and alkylation of toluene with benzyl chloride gave selectively p-benzyl toluene (PBT). Results are presented in Table 2.14. Further, for comparative study, at this optimized condition Al-MCM-41-30 is used as solid acid catalyst for synthesis of 3,4DMA, 4MA and PBT. The results are presented in Table 2.14.
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When comparison is made between anisole and veratrole the product yield and turn over number (TON) are higher for veratrole. The rate-determining step of the Friedel-Crafts acylation is the formation of the electrophilic intermediate. The presence of an additional electron donating methoxy group in veratrole makes it a more active compound for electrophilic substitution of acyl group in the para position than anisole due to an increased electron density at para position and resultant increased susceptibility for attack by the electrophile.

It is reported that the mechanism for Friedel-Crafts acylation and alkylation over solid acid catalysts is the same as homogeneous Lewis acid catalysts, [197,202,203]. The proposed mechanism for the acylation and alkylation reaction on solid acid catalyst implies the formation of an adsorbed species by interaction of the acylating/alkylating agent with a Brønsted acid site [202,203] (acyl/alkyl cation). The Brønsted acid site generates an acyl carbonium ion, which in turn affects the electrophilic substitution. A higher density of acid sites increases number of acyl cations enhancing activity of the reaction. Catalytic activity is a function of number as well as type of acid sites present on the catalyst surface. The acylation and alkylation reactions are thus driven by the surface acidity of the catalyst. Probably this is the reason why 12TPA-MCM-41-20 gives higher yields compared to Al-MCM-41-30 due to higher surface acidity observed in case of the former catalyst. In an earlier study using TMA salts as solid acid catalyst in Friedel-Crafts acylation and alkylation a probable mechanism [230,231] has been proposed by us, as given in Scheme 2.9 and 2.10. The same mechanism is thought to be operating in the present study.

% yields obtained in recycled catalyst and % decrease in yields in subsequent cycles is presented in Table 2.14 and 2.15 respectively, and a graphical presentation (Fig. 2.48). It is observed that in subsequent cycles decrease in % yields is less for Al-MCM-41 compared to 12TPA-MCM-41-20. This could be due to the leaching of 12TPA from surface of MCM-41. It is observed that the colour of the catalyst changes after each catalytic run.
**Scheme 2.9** Reaction mechanism of Friedel-Crafts acylation of anisole using solid acid catalyst.

**Scheme 2.10** Reaction mechanism of Friedel-Crafts alkylation of toluene using solid acid catalyst.
This gives an indication that during the course of the reaction the reacting molecules come onto the surface of the catalyst. Some of them enter into reaction to give the product while a few of them get adsorbed on the surface, which is marked by the change in the colour of the catalyst. The fact that the reactant molecules are weakly adsorbed is evident from the catalyst regaining its original colour, when treated with ethanol. The possibility of molecules entering interstices cannot be ruled out. This is observed from the fact that the yields go down by 3-6% after every regeneration, leading to deactivation of the catalyst. The deactivation of the catalyst might be due to the strongly adsorbed acetic acid and the product on the acid sites. It is known that acetic acid is generally strongly absorbed on the acidic sites. The above two reasons are responsible for decrease in % yield.
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Fig. 2.48 Comparative catalyst performance in the Friedel-Crafts alkylation and acylation

Table 2.13 Optimization of reaction conditions for Friedel Crafts acylation and alkylation using 12TPA-MCM-41-20

<table>
<thead>
<tr>
<th>No</th>
<th>Reactants with mole ratio</th>
<th>Catalyst Amount (g)</th>
<th>Time (h)</th>
<th>Temp. (°C)</th>
<th>% Yield of 3,4DMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Time variation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>V: AA (1:1.5)</td>
<td>0.10</td>
<td>1</td>
<td>70</td>
<td>47.46</td>
</tr>
<tr>
<td>2</td>
<td>V: AA (1:1.5)</td>
<td>0.10</td>
<td>2</td>
<td>70</td>
<td>53.69</td>
</tr>
<tr>
<td>3</td>
<td>V: AA (1:1.5)</td>
<td>0.10</td>
<td>3</td>
<td>70</td>
<td>55.69</td>
</tr>
<tr>
<td>4</td>
<td>V: AA (1:1.5)</td>
<td>0.10</td>
<td>4</td>
<td>70</td>
<td>61.55</td>
</tr>
<tr>
<td>5</td>
<td>V: AA (1:1.5)</td>
<td>0.10</td>
<td>5</td>
<td>70</td>
<td>60.85</td>
</tr>
<tr>
<td>6</td>
<td>V: AA (1:1.5)</td>
<td>0.10</td>
<td>6</td>
<td>70</td>
<td>61.35</td>
</tr>
<tr>
<td>B</td>
<td>Catalyst amount variation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>V: AA (1:1.5)</td>
<td>0.15</td>
<td>4</td>
<td>70</td>
<td>69.42</td>
</tr>
<tr>
<td>8</td>
<td>V: AA (1:1.5)</td>
<td>0.20</td>
<td>4</td>
<td>70</td>
<td>74.33</td>
</tr>
<tr>
<td>9</td>
<td>V: AA (1:1.5)</td>
<td>0.25</td>
<td>4</td>
<td>70</td>
<td>74.47</td>
</tr>
<tr>
<td>C</td>
<td>Mole ratio variation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>V: AA (1:0.75)</td>
<td>0.20</td>
<td>4</td>
<td>70</td>
<td>47.80</td>
</tr>
<tr>
<td>11</td>
<td>V: AA (1:1)</td>
<td>0.20</td>
<td>4</td>
<td>70</td>
<td>53.54</td>
</tr>
<tr>
<td>12</td>
<td>V: AA (1:2)</td>
<td>0.20</td>
<td>4</td>
<td>70</td>
<td>74.31</td>
</tr>
<tr>
<td>D</td>
<td>Temperature variation</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>V: AA (1:1.5)</td>
<td>0.20</td>
<td>4</td>
<td>100</td>
<td>73.45</td>
</tr>
<tr>
<td>14</td>
<td>V: AA (1:1.5)</td>
<td>0.20</td>
<td>4</td>
<td>120</td>
<td>72.49</td>
</tr>
</tbody>
</table>

A = Anisole; AA = Acetic Anhydride; V = Veratrole; T = Toluene; BzCl= Benzyl Chloride
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Table 2.14 Friedel Crafts acylation and alkylation using 12TPA-MCM-41-20 and Al-MCM-41-30 at optimized condition

<table>
<thead>
<tr>
<th>No</th>
<th>Reactants</th>
<th>Product</th>
<th>Temp. (°C)</th>
<th>12TPA-MCM-41-20</th>
<th>Al-MCM-41-30</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>% Yields</td>
<td>*TON</td>
<td>% Yields</td>
</tr>
<tr>
<td>1</td>
<td>V: AA</td>
<td>3,4DMA</td>
<td>70</td>
<td>74.33</td>
<td>10.81</td>
</tr>
<tr>
<td>2</td>
<td>A: AA</td>
<td>4MA</td>
<td>70</td>
<td>59.39</td>
<td>9.00</td>
</tr>
<tr>
<td>3</td>
<td>T: BzCl</td>
<td>PBT</td>
<td>110</td>
<td>72.02</td>
<td>9.82</td>
</tr>
</tbody>
</table>

Catalyst reusability

<table>
<thead>
<tr>
<th>No</th>
<th>Reactants</th>
<th>Product</th>
<th>Temp. (°C)</th>
<th>12TPA-MCM-41-20</th>
<th>Al-MCM-41-30</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>% Yields</td>
<td>*TON</td>
<td>% Yields</td>
</tr>
<tr>
<td>1</td>
<td>V: AA 1st Cycle</td>
<td>3,4DMA</td>
<td>70</td>
<td>72.89</td>
<td>10.62</td>
</tr>
<tr>
<td>2</td>
<td>V: AA 2nd Cycle</td>
<td>3,4DMA</td>
<td>70</td>
<td>68.37</td>
<td>10.05</td>
</tr>
<tr>
<td>3</td>
<td>A: AA 1st Cycle</td>
<td>4MA</td>
<td>70</td>
<td>56.40</td>
<td>8.20</td>
</tr>
<tr>
<td>4</td>
<td>A: AA 2nd Cycle</td>
<td>4MA</td>
<td>70</td>
<td>51.63</td>
<td>7.10</td>
</tr>
<tr>
<td>5</td>
<td>T: BzCl 1st Cycle</td>
<td>PBT</td>
<td>110</td>
<td>66.15</td>
<td>10.00</td>
</tr>
<tr>
<td>6</td>
<td>T: BzCl 2nd Cycle</td>
<td>PBT</td>
<td>110</td>
<td>61.74</td>
<td>9.45</td>
</tr>
</tbody>
</table>

A = Anisole; AA = Acetic Anhydride; V = Veratrole; T = Toluene; BzCl= Benzyl Chloride;
Catalyst amount = 0.20g; reaction time = 4 h. mole ratio of the reactants = 1:1.5 (Veratrole/Anisole/Toluene:acylating/alkylating agent); *TON = Turn over number, gram of product formed per gram of catalyst.

Table 2.15 % Decrease in yields of 3,4DMA, 4MA and PBT using recycled catalysts in subsequent cycles

<table>
<thead>
<tr>
<th>Product</th>
<th>% Decrease in yields</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>12TPA-MCM-41-20</td>
</tr>
<tr>
<td></td>
<td>1st Cycle</td>
</tr>
<tr>
<td>3,4DMA</td>
<td>2</td>
</tr>
<tr>
<td>4MA</td>
<td>3</td>
</tr>
<tr>
<td>PBT</td>
<td>5</td>
</tr>
</tbody>
</table>

2.21 CONCLUSIONS

In the present study, Green Chemistry goals have been achieved by using solid acid catalysts (replacing liquid acid catalysts used in conventional reactions) and under solvent free conditions with high selectivity of the products. The products formed can be simply distilled over, there is no catalyst contamination in product and no acid waste formed. The catalyst can be regenerated and reused. Further, since the studied reactions are driven by surface acidity of the catalyst, there is scope to obtain higher/better yields by synthesizing materials with higher surface acidity. Finally, the MCM-41 neutral framework has been successfully modified and put to practical use.
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