CHAPTER I
BACKGROUND AND LITERATURE SURVEY

1.1 Introduction

In recent years, there have been dramatic advances in the concept of molecular sieves exhibiting uniform pore sizes. Pores are classified according to pore diameter, as follows: micropores have diameter less than 2 nm, mesopores have diameter between 2 and 50 nm and macropores have diameters greater than 50 nm (Beck et al., 1992). Amorphous mesoporous materials represent an important class of porous inorganic solids having no long-range order and usually having a wide distribution of pore sizes. In contrast, microporous molecular sieves have a crystalline structure with a very narrow pore size distribution. It is generally presumed that a mesoporous material with uniform pores would have wide utility in catalysis. Therefore, considerably synthetic effort has been devoted to develop frameworks with pore diameters within the mesoporous range. MCM-41, one of the mesoporous materials, composes of amorphous silica, however, it displays an ordered structure with uniform mesopores arranging into a hexagonal, honeycomb-like lattice. The best example of this structure can be seen in figure 1.1. In this figure one looks directly inside the uniform mesopores, which are separated from each other by thin walls of amorphous silica, approximately 1 – 1.5 nm thick [5, 20, 38].

It is not necessary for mesopores to align in a straight way throughout the silica matrix. They can be slightly curved, thereby retaining the hexagonal ordering, as can be seen in figure 1.2.
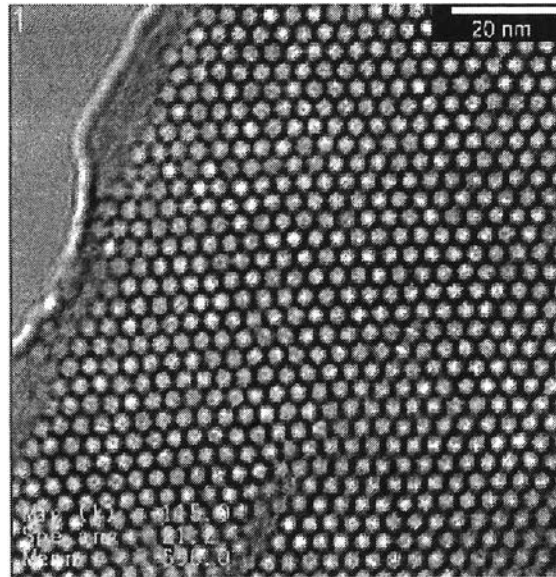
Figure 1.1   TEM micrograph of MCM-41, showing the arrangement of mesopores in a honeycomb-like structure, separated by thin, amorphous silica pore walls (black) [20].

Figure 1.2   TEM micrograph of MCM-41, showing the slightly curved uniform mesopores running through the silica matrix [20].

From the micrographs it is apparent that MCM-41 has a very large void fraction, due to the presence of the mesopores, and a rather low density [5,8,20]. As a result, MCM-41 displays a very large specific surface area of 1,000 m^2g^{-1} approximately. This property makes MCM-41 very interesting to be used as support material for heterogeneous catalysts. Moreover, because MCM-41 exclusively contains mesopores it can both provide access to large molecules and alleviate diffusion problems, which are frequently encountered in microporous materials, such as zeolites [3,5,8,42]. It should be noted, however, that the one-dimensional nature as well as the relatively large length of the mesopores (usually extending over several hundreds of nanometers) could also give rise to transportation limitations.

Despite the advantages mentioned above there is one eminent drawback associated with MCM-type materials, *viz.* the rather limited stability, which is a result of the very thin, amorphous pore walls. Because of a very large mesopore surface area the pore walls are extremely reactive towards a number of agents, resulting in the collapse of the thin walls upon exposure to these agents. From a viewpoint of application the instability of silica support materials (either co-fed as diluents or produced during catalysis) towards steam, resulting in the chemical evaporation of silica, makes silica-supported catalysts inappropriate for a rather large range of processes [3,8,37,42]. Furthermore, there is a notable instability of MCM-41 towards mineralizing agents, *i.e.* hydroxide and fluoride ions because these agents dissolve silica. As a result, the stability of MCM-41 in aqueous solutions is limited to pH values ≤ 7. Moreover, the chemical affinity of the pore surface towards precursors of catalytically active phases sometimes results in the collapse of the hexagonal framework structure.

Many researchers have tried to introduce a second cation, such as a transition metal, into the silica-based MCM-41 framework and have used them as effective catalysts for various kinds of reactions. MCM-41 has various flexible framework structure, compared to crystalline zeolites, allowing various kinds of metal to be incorporated into the silica framework without collapse of its basic structure when the preparation conditions are carefully controlled. The vanadium-substituted MCM-41

materials were found to be very active catalysts in the selective oxidation of hydrocarbons using H_2O_2 in liquid phase reaction, especially for larger molecules [3,37].

1.2 Synthesis

MCM-41 can be synthesized following a wide variety of preparation procedures. However, there is one thing that all these procedures have in common next to the obvious presence of a silica source, *viz.* a templating agent [7,19,37]. A template is a structure-directing a gent, which is usually a relatively simple molecule or ion, around which a framework is built up. The most common templates are quaternary ammonium ions with short alkyl chains, which are used for the synthesis of a large number of zeolites [7,19,31,40]. Similar to the synthesis of MCM-41 quaternary ammonium ions are frequently used, albeit with one important modification: at least one of the short alkyl chains is replaced by a long alkyl chain, generally a hexadecyl group. This slight modification has an enormous impact on the behavior of the template in aqueous solutions [9]. However, due to the large hydrophobic alkyl chain the template ions will aggregate t ogether t o minimize e nergetically u nfavorable i nteractions of t he non-polar alkyl chains with very polar water solvent molecules. This is exactly the same behavior as displayed by soaps upon d issolution i n w ater. T he r esulting a ggregates o f i ons a re denoted *micelles*. It follows that these micelles have a hydrophobic core, containing large alkyl chains, and hydrophilic surface, due to the ionic character of the ammonium head groups [9,31,40].

The most energetically favorable form of micelles is spherical because in t his geometry the surface energy is most efficiently minimized. Moreover, this conformation allows the largest number of micelles to be formed, which is attractive considering the entropy of the system. Nevertheless, it is observed that at increasing amounts of template in water different micelle geometry evolves: the spherical micelles gradually transform into long tubes, often denoted as rod-like micelles [40]. Further increase in the template concentration results in aggregation of the rod-like micelles into a hexagonal *liquid*

crystalline structure, resembling the MCM-41 structure. If the template concentration is increased further this hexagonal liquid crystalline phase first transforms into a cubic liquid crystalline phase and eventually, at the highest template concentrations, into a lamellar liquid crystalline phase. The cubic liquid crystalline phase resembles the structure of mesoporous MCM-48, where as the lamellar phase is the structural analogue of MCM-50 (an unstable material, which consists of platelets of amorphous silica) [4,34]. Because of the resemblances between the liquid crystalline phases and the MCM structures it is often assumed that the liquid crystalline structures are the actual templates of MCM-41 and MCM-48. In the case of MCM-48 this is indeed the most likely templating mechanism. However, in a large number of studies that were devoted to the elucidation of the mechanism of MCM-41 formation the hexagonal liquid crystalline phase was initially not observed in the synthesized gels although MCM-41 was formed. These findings imply that another mechanism can be operative as well in the formation of MCM-41. In this alternative mechanism the rod-like micelles assemble not prior to but during the generation of the MCM-41 structure [13,25,36,40,43]. A convincing explanation for this behavior is that the aggregation of the rod-like micelles into a liquid crystalline structure is thought to be energetically unfavorable, due to the electrostatic repulsions between the positively charged surfaces of the micelles (electrical charges are a result of the presence of the ionic head groups). During synthesis of MCM-41 the electrostatic repulsions decrease as a result of the formation of a monolayer of silica around the micelles, thereby facilitating the subsequent aggregation of the micelles into close-packed hexagonal structures.

Next to a structure-directing agent and water as a solvent two more ingredients are required for the synthesis of MCM-41: a source of silica and a mineralizing agent. Various source of silica can be used for synthesis, *viz.* water glass, amorphous silica and Kanemite (a layer silicate structure consisting of anionic silica sheets with charge-compensating sodium ions present in the interlayers) [12,23-24]. Furthermore, organic silicon alkoxides are also frequently used. For the dissolution of the various silica sources a so-called "mineralizing agent" is used. For this purpose sodium hydroxide or

concentrated ammonia solution are frequently used, although HF also finds application, despite the hazards associated with its use. Upon dissolution of silica by the mineralizing agent small silicon oxy-anions are produced. In the presence of the rod-like template micelles the silicate anions diffuse towards the surfaces of the micelles as a result of eletrostatic attractions [4,25,34]. Therefore, the concentration of silicate anions at the surface of the micelles rapidly increases, as do the electrostatic repulsions between the individual silicate ions. In order to alleviate these repulsive interactions the silicate ions start to condense with each other, thereby forming a monolayer of amorphous silica around the micelles. Charge compensation of the ionic head-groups of the template is still brought about by deprotonated silanol groups of the silica monolayer. At this stage the silica "coated" micelles can start to cluster together by condensation reactions between the silica layers of individual micelles, thus generating the MCM-41 framework. As a result of these processes the pore walls of MCM-41 are amorphous and only 2-3 monolayers thick [12-13,23,25,36,43].

The processes described above can take place over a wide range of synthesis conditions, including gel composition, pH, timescale, temperature and pressure [13]. However, once MCM-41 has been formed its pores are filled with template and in order to obtain a completely mesoporous support material the micelles must be removed. The most elegant solution to this demand is removal by means of (repeated) washing with (slightly acidified) mixtures of organic solvent and water, resulting in extraction of the template. A simpler method for template removal is calcinations. During this process template is decomposed into CO_2, some NO_x and steam. Although MCM-41 is unstable with respect to steam, the quantities of steam produced during this process are too small to do any damage to the MCM-41 framework structure.

1.3 The Sol-Gel Process

The conventional synthesis of ceramic materials involves the direct reaction of a mixture of powders. For these solid state reactions, high temperature and small particle

sizes are needed to provide high mobility of the reactants and maximum contact surface between the particles [34]. Several difficulties have to be considered: thermodynamic factors often prevent metastable phase formation, control over the size and morphology of solid particles is almost impossible, the stoichiometry is difficult to reproduce, impurities of reactant, poor chemical homogeneity and the formation of undersirable phases are also obtained.

In the field of ceramics, chemistry has two major roles. It has to provide not only methods for the synthesis of novel ceramics, but also techniques for the fabrication of these materials into useful shapes. Thus, new synthesis methods have been developed [13,25,36,43].
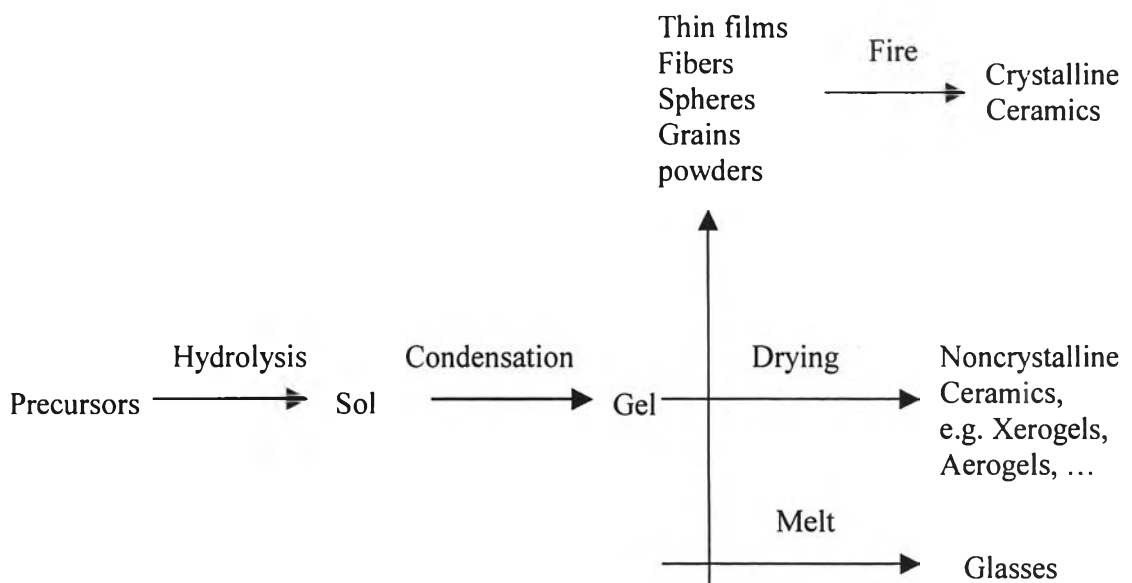
Among these chemical methods like coprecipitation (formation of intermediate precipitates with the correct stoichiometry), reactions in molten salts (molten salts as solvent), hydrothermal techniques, polymer pyrolysis (synthesis of a polymeric compound, which is then fabricated into a shape and pyrolysed to the ceramic), topochemical and ion-exchange reactions, especially sol-gel process has been extensively studied [9,20]. Starting from molecular precursor, an oxide network is obtained via inorganic polymerization reactions. Since these reactions occur in solution, sol-gel processing broadly describes the synthesis of inorganic oxides by wet chemistry methods. Compared to the conventional powder route, sol-gel process allows a better control from the molecular precursor to the final product, offering possibilities in the tailoring of materials which result in high purity, high homogeneity, low temperature preparations, size and morphological control of the particles, and the opportunity for the preparation of new crystalline and non-crystalline solids [3,19,37,42].

In general, the sol-gel procedure consists of the following step (Scheme 1.1):

1. Preparation of homogeneous solution either by dissolution of metal organic precursors in an organic solvent that is miscible with water, or by dissolution of inorganic salts in water.

2. Converting the homogeneous solution to a sol by treatment with a suitable reagent (pure water or water with either HCl, NaOH or NH$_4$OH)

3. Aging: the sol changes into a gel by self-polymerization
4. Shaping the gel to the finally desired form (thin films, fiber, spheres...)
5. Converting (sintering) the shaped gel to the desired ceramic material generally at temperature around 500°C.

The most important step in this route is the formation of an inorganic polymer by hydrolysis reactions, *i.e.* the transformation of the molecular precursor into a highly crosslinked solid. Hydrolysis leads to a sol, a dispersion of colloidal particles (solid particles with diameters of 1-100 nm) and condensation forms a gel, and interconnected, porous network filled with a liquid phase. This transformation is called the sol-gel transition [19,31]. During removal of the pore liquid under hypercritical conditions, the network does not collapse and aerogels are produced. When the pore liquid is removed by evaporation under normal conditions, shrinkage of the pores occurs and xerogel is formed. One of the highly attractive features of the sol-gel process is the possibility to obtain the final ceramic materials in different form like fibers, coating, spheres, irregular aerogels and others by the control of the process conditions [40].

Thin films
Fibers   Fire
Spheres   ─────────────▶ Crystalline
Grains   Ceramics
powders

                              ▲

                        Drying   Noncrystalline
Precursors ──Hydrolysis──▶ Sol ──Condensation──▶ Gel ──────────▶ Ceramics,
                                                                      e.g. Xerogels,
                                                                      Aerogels, ...

                        Melt
   ────────────▶ Glasses

Scheme 1.3   Complete Process of Ceramic and Glass Production.

The sol-gel process can be classified into two different routes depending on the nature of the precursors: a) the precursor is an aqueous solution of an inorganic salt or b) a metal organic compound. The inorganic route involves the formation of condensed species from aqueous solutions of inorganic salts by adjusting pH, by increasing the temperature or by changing the oxidation state [5,8]. However, this method has several disadvantages. The aqueous chemistry of transition metal ions can be rather complicated because of the formation of a large number of oligomeric species, depending on the oxidation state, the pH or the concentration. The role of the counter anions, which are able to coordinate the metal ion giving raise to a new molecular precursor with different chemical reactivity towards hydrolysis and condensation, is almost impossible to predict. These ions can influence the morphology, the structure and even the chemical composition of the resulting solid phase. Also the removal of these anions from the final metal oxide product is often a problem. In addition, the formation of a gel rather than a precipitate from inorganic precursors is very complicated, depending on pH, concentration, addition mode, order of reactant mixing, temperature, chemical composition of the aqueous solution, and even the geometry of the reaction vessel plays a role [3,8,37,42].

In order to avoid all these problems, in many cases metal alkoxides are used for the preparation of metal oxides. Metal alkoxides are strongly preferred as precursors because they are soluble in organic solvent providing high homogeneity, they can easily be converted to the corresponding oxide [31]. The disadvantages are that only a few are commercially available and that they are in general very expensive.

The sol-gel process involving metal alkoxides is normally based on hydrolysis and condensation reactions. These nucleophilic reactions can be described as the substitution of alkoxy ligands by hydroxylated species, XOH, as follows [9]:

$$M(OR)_z + y\,XOH \xrightarrow{-\,y\,ROH} [M(OR)_{z-y}(OX)_y] \xrightarrow{\Delta T} MO_x$$
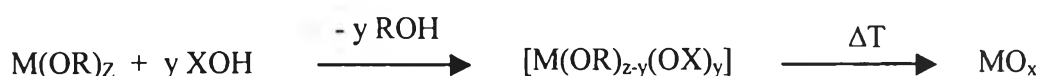
where X stands for hydrogen (hydrolysis), a metal atom (condensation), or even an organic or inorganic liquid (complexation). Finally, heat treatment of the wet gel results in the formation of the corresponding metal oxide. In this step, the amorphous network is first dried and then solidified.

Chemical aspects play an important role in studying and controlling the sol-gel process. The chemical reactivity of metal alkoxides towards hydrolysis and condensation depends mainly on the electronegativity of the metal atom, its ability to increase the coordination number, the steric hindrance of the alkoxy group, and on the molecular structure of the metal alkoxides (monomeric or oligemeric) [9]. The amount of added water in the hydrolysis step and how the water is added, determine whether the alkoxides are completely hydrolyzed and which oligemeric intermediate species are formed. Additional parameters are the polarity, the dipole moment, and the acidity of the solvent. The large amount of different reaction parameters as well as the simultaneous occurrence of hydrolysis and condensation reactions, still prevents reliable methods to control complete sol-gel transformation [34].

1.4 Characterization

Although a variety of techniques exist for the characterization of heterogeneous catalysts and support materials, MCM-41 is most frequently studied with nitrogen physisorption and x-ray diffraction. Therefore, only these two techniques will herein be dealt with.

First of all, the application of x-ray diffraction for the characterization of a basically amorphous material appears to be rather useless, since x-ray diffraction is always used to attain information on crystalline materials. Nevertheless, the prerequisite for x-ray diffraction is that the materials studied display long-range structural ordering and it can be seen in figure 1 that MCM-41 presents a well-ordered lattice. Moreover, because of the geometry of its lattice MCM-41 can be indexed with a hexagonal unit cell, with a = b and c = ∞ [3,5,8,20,25,42]. Because the parameters a and b are in the

order of nanometers instead of tenths of nanometers, as usually encountered in crystals, x-rays are diffracted over small angels only. Therefore, characterization of MCM-41 with x-ray diffraction yields a diffractogram with a limited number of reflections situated at low angles. A representative example can be seen in figure 1.3. Generally, only three diffractions are well-resolved, c orresponding to the (100), (110) and (200) reflections. A f ourth d iffraction p eak w ith a notably lower intensity, corresponding to the (210) reflection, is rarely present [5,20,38].
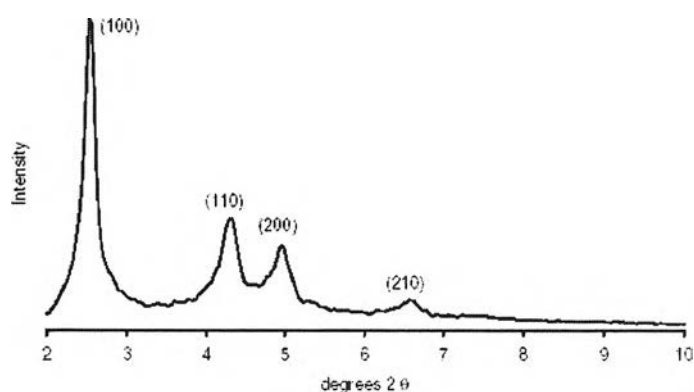

Figure 1.4   X-ray diffractogram of MCM-41 showing four reflections, which can be assigned to the hexagonal lattice of the mesoporous material [20].

When a n M CM-41 m aterial of exceptionally good quality has been obtained a fifth diffraction peak, corresponding to the (300) reflection, is also observed. From the reflection angles the size of the hexagonal unit cell of MCM-41 can be calculated (*i.e.* the parameters a and b). With these values and the pore diameter (determined with nitrogen p hysisorption) t he thickness of the silica pore walls can easily be calculated. The value thus obtained is a good measure for the thickness of the pore walls close to 1.5 nm, but values as low as 0.8 nm have been reported [5,20,38].

Nitrogen physisorption probes the textural properties of materials, *i.e.* surface area, pore volume, pore size (distribution) and pore geometry. Moreover, the technique also discloses to what extent the measured surface area associated with micro-, meso-

and / or macropores. A typical nitrogen isotherm for MCM-41 is shown in figure 1.4 [5,8,20].

Both the adsorption (straight line) and desorption (dotted line) curves are shown. Five distinct regions can be discerned in this graph. At very low relative pressures (p/p_0) a very large amount of nitrogen becomes physisorbed (region I). Nitrogen physisorption at these low pressures is usually assigned to condensation of nitrogen inside the micropores of a material. However, as outlined before, MCM-41 is a completely mesoporous material and does not contain any micropores. Therefore, the process taking place in region I is monolayer adsorption of nitrogen on the surface of MCM-41 (both on the external surface and inside the mesopores). Because the surface area is very high the concomitant monolayer adsorption requires a large amount of nitrogen [8,42]. Upon monolayer adsorption, multilayer of nitrogen starts to develop at higher relative pressures of nitrogen (region II). Also in this case both the external surface area and the mesopores contribute to the physisorption process. Therefore, the data collected in this part of the isotherm are used for the calculation of the surface area of the material with the method developed by Brunauer, Emmett and Teller (BET-method) [8,42].
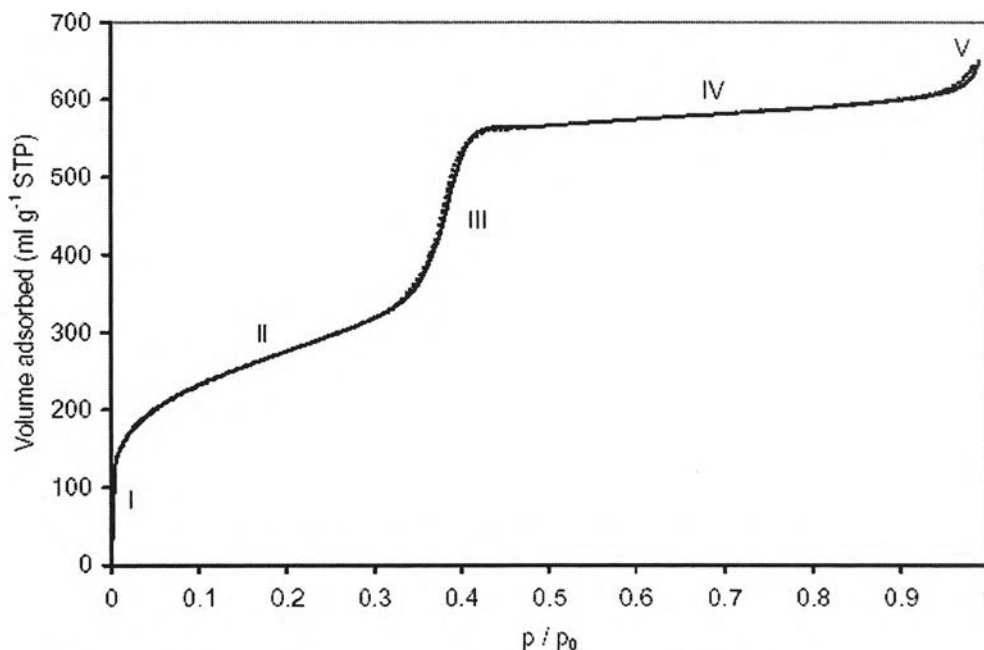
Figure 1.5   Nitrogen isotherm for all-silica MCM-41. The straight line is the adsorption curve an the dotted line is the desorption curve [5].

At a relative nitrogen pressure of approximately 0.37 a sudden steep increase of the amount of adsorbed nitrogen is observed (region III). This steep increase is caused by capillary condensation of nitrogen inside the mesopores, *i.e.* the mesopores of MCM-41 become suddenly filled by liquid nitrogen since the meniscus of the liquid nitrogen film inside the mesopores becomes thermodynamically unstable at this pressure. The Kelvin equation relates the pore diameter of a material with the relative pressure at which capillary condensation occurs [5,8,31]. Because filling of the mesopores takes place over a relatively small range of relative pressures (*i.e.* $p/p_0 \approx 0.34 - 0.40$) the pores associated with this process must all be nearly equal in size (which is indeed the case, as is apparent from figure 1.1). A further indication for this statement is the fact that the desorption curve almost completely coincides with the adsorption isotherm in this pressure range, giving a very narrow hysteresis loop (*i.e.* the difference between the adsorption and desorption curves). Moreover, the shapes of the curves and the hysteresis

loop are unique characteristic for cylindrical mesopores, which indeed constitute the MCM-41 structure (see figure 1) [8,40,42].

When the mesopores have become completely filled with nitrogen, only the external surface of MCM-41 remains accessible for nitrogen adsorption. Therefore, region IV is associated with multiplayer adsorption of nitrogen at the external surface of MCM-41. The very shallow slope of this region indicates that the external surface area of MCM-41 is rather small. Finally, at relative pressures close to 1 the nitrogen uptake by the sample increases again and a small hysteresis loop evolves upon the subsequent desorption of nitrogen (region V). These features can be assigned to condensation of nitrogen within the interstitial voids between the MCM-41 particles [19].

As described earlier, the vanadium-substituted MCM-41 materials were very active catalysts. The UV-vis spectroscopy is generally used to characterize vanadium electron transfer of V(V) ions. The lower energy charge-transfer (LCT) band for octahedral coordination is falling in the 333-500nm region. In tetrahedral vanadium compounds, in contrast, the LCT band is found at 333 nm and the second charge-transfer (CT) transition band appears at 278 nm. The LCT transition for V(IV) falls at lower wavelength in the 250-286 nm region, whereas the d-d transitions of VO^{2+} ions fall in the region of 769 nm. The d-d transition at higher wavelength is generally masked by more intense charge-transfer transitions [7,19,40].

1.5 Literature Review

In 1992, researchers at Mobil Research and Development Corporation reported the exciting discovery of the novel family of molecular sieves called M41S (MCM-41, MCM-48 and MCM-50) [5,20,38]. The original M41S family of mesoporous molecular sieves was synthesized, in general, by the combination of appropriate amounts of a silica source (e.g. tetraethylorthosilicate (TEOS), Ludox, fumed silica, sodium silicate), an alkyltrimethylammonium halide surfactant [7] (e.g. cetyltrimethylammonium bromide (CTAB)), a base (e.g. sodium hydroxide or Tetramethylammonium hydroxide

(TMAOH)), and water. Aluminosilicate M41S was synthesized by the addition of an aluminum source to the synthesis mixture. The mixture was aged at elevated temperature ($\geq$ 100°C) for 24 to 144 hr, which resulted in a solid precipitate. The organic-inorganic mesostructured product was filtered, washed with water and air-dried. The product was calcined at about 500°C under a flowing gas to burn off the surfactant, to yield the mesoporous material. Many research groups [37] all over the world exploited this technique of supramolecular templating to produce not only mesoporous silicate and aluminosilicate materials, but also mesostructured metal oxides. The extension of this liquid-crystal templating (LCT) mechanism into the field of transition metal oxide synthesis represented a major step forward towards tailoring catalytic, electronic and magnetic properties of these redox-active materials [37].

The influence of alkyl chain length and the addition of mesitylene on the pore size has been taken as strong evidence for the LCT mechanism, since this phenomenon is consistent with the well-documented surfactant chemistry [7,19,40]. The auxiliary organic species added to the reaction gel can be solubilized inside the hydrophobic regions of micelles, causing an increase in micelle diameter so as to increase the pore size of MCM-41. The observed pore size increase of the aluminosilicates compared to the siliceous MCM-41 was due to the replacement of the shorter Si-O bonds (1.6 °A) by the longer Al-O bonds (1.75 °A) [25,36].

Huo et al. (1994b) and Firouzi et al. (1995) suggested that ion exchange between surfactant anions (OH-, Br-, Cl-) and multiply charged anionic silica oligomer (D4R, D3R) may take place in a surfactant-silicate aqueous solution. This multidentate bonding can screen the intraaggregate electrostatic head group repulsions so as to reduce the average head group area of the surfactants. The collective results can further decrease the local curvature of the aggregate, which implies that the cooperative assembly of inorganic-organic species is formed with structures different from that of the precursor micelles.

In 1994, Sayari reported the possibility of preparing V-incorporated MCM-41. In 1997, P. I. Ravikovitch used V_2O_5 to prepare V-MCM-41 that has more uniform

structure than the procedure using $VOSO_4.3H_2O$ solution. However, there are few results claiming neither successful preparation of V-MCM-41 with high reproducibility and mechanical stability nor having a systematic investigation of acidic properties relevant to catalytic applications.

1.6 Objectives

The objectives of this research work are to study the synthetic methods of high surface area MCM-41 directly from our synthesized silatrane precursor and vanadium loaded MCM-41, including product characterization.