# **CHAPTER 1. GENERAL INTRODUCTION**

## **1.1. Extension from Microporous to Mesoporous Dimensions**

According to the IUPAC system [1], porous materials are classified according to their pore sizes into three classes: (i) Microporous, having pore sizes below 20 Å; (ii) Mesoporous, with intermediate pore sizes in the range 20 - 500 Å; and (iii) Macroporous, with pore sizes exceeding 500 Å.

Zeolites and zeolite-like molecular sieves belong to the microporous class, and have attracted particular attention in the fields where molecular recognition is needed, e.g. catalysis, separations and chemical sensing [2, 3]. They have been extensively used in acid-catalyzed reactions for the production of petrochemicals and fine chemicals, where they serve both as catalysts and catalyst supports. Their extensive usage was prompted by attractive features like their high thermal and hydrothermal stability, as well as tunable acidity. However, the limitation in the applicability of zeolite catalysts and supports lies in the diffusional constraints (so-called shape selectivity) in reactions involving bulky reactants or those generating bulky products because of the restricted pore sizes. The need to extend zeolitic dimensions beyond this shape-selective limit, i.e., making zeolites with pores comprised of larger than 12 T-atoms (pore diameters 6-8 Å), has seen much research effort. Pore systems that contain rings circumscribed by more than 12 T-atoms are classified as extra-large pores [4].

One of the initial attempts to improve the diffusion of reactants involved the use of pillared clays (PILCs), prepared by intercalating voluminous metallic complexes between structural layers of swelling clays like smectites in order to separate the layers [5-10]. Although the resulting materials possess high surface area and large interlayer separations, they are still of limited practical utility [11].

Another attempt involved synthesizing zeolites and/or zeotypes comprising larger ring sizes than conventional zeolites. In this light, the first molecular sieve with extralarge pores was an aluminophosphate material with 18-membered ring pores and three-dimensional topology, designated VPI-5 [12]. Its silicon-containing analogue, MCM-9, was reported immediately thereafter [13]. Subsequently, the synthesis of two other phosphate-based extra-large pore materials with 20-membered rings were reported, cloverite (14) and JDF-20 [15, 16], which are grouped with the naturally occurring 20-membered ring phosphate, cacoxenite [17]. The main shortcoming of these phosphate-based molecular sieves is the lack of the desired properties of combined high acidity and thermal/hydrothermal stability, which limits their practical potential.

Recently, the first extra-large pore zeolite with 14-membered ring size, designated UTD-1, was reported and shown to possess good acidity and thermal/hydrothermal stability [18, 19]. This extra-large pore zeolite, with a DON-type structure and a ring size of 14 tetrahedral atoms, was synthesized using an organometallic structure-directing agent (SDA), the bis(pentamethylcyclopentadienyl)cobalticenium cation. Another 14-membered ring material with one-dimensional pores, high-silica CIT-5 with a CFI-type structure, has been subsequently synthesized under hydrothermal conditions in the presence of N(16)-methylsparteinium and Li<sup>+</sup> [20, 21].

To summarize this endeavour of preparing large pore materials with open-framework structures, it can be stated that while a ring size of only 14 tetrahedral atoms in known in zeolites, extra-large pore phosphates come with various ring sizes, including 14, 16, 18, 20 and 24. Unfortunately phosphate-based molecular sieves have lower thermal stability.

Recently, Corma and coworkers [22, 23] realized that, as in layered clay materials, zeolites can be delaminated to improve the accessibility of catalytic sites to large molecules.

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Another conventional approach to prepare molecular sieve materials with larger pore sizes is the so-called "secondary synthesis method". In this method, microporous zeolite molecular sieves such as A, X, and Y were chemically treated with a  $(NH_4)_2SiF_6$  solution or steamed. Such a treatment generated mesopores but the pore sizes of these treated materials did not have a narrow distribution [24].

A remarkable breakthrough in the templated synthesis of large-pore zeolites was the discovery of the M41S family of mesoporous materials which were synthesized by researchers at the Mobil Research and Development Corporation (Ltd) [25, 26]. These materials show a very narrow pore size distribution. The members of this family are MCM-41, MCM-48 and MCM-50, which differ from each other in their unit cell types and overall crystallographic point groups. MCM-41 is hexagonal, MCM-48 is cubic (space group *Ia*3*d*) while MCM-50 is lamellar. The formation of each of these phases is dependent on the synthesis conditions, particularly the surfactant to silica molar ratio of the synthesis gel. This discovery of the M41S family of materials has, therefore, dramatically expanded the range of pore sizes from micropore (13 Å) to mesopore (20-100 Å), with MCM-41 being the most studied member of the M41S family. The Mobil researchers have named the formation mechanism of the MCM series of materials a "liquid crystal templating" (LCT) mechanism. It involves electrostatic interaction between quaternary ammonium salts  $[C_nH_{2n+1}(CH_3)_3NBr]$  and the silicate polyanion. The phases that result from the LCT mechanism involving silicates and amphiphilic alkyltrimethylammonium surfactants are depicted in Figure 1.1:



Fig. 1.1. Three structure types observed for silica-surfactant mesophases : (a) MCM-41 (Hexagonal, 1-D), (b) MCM-48 (Cubic, bicontinuous, 3-D), (c) MCM-50 (Lamellar, 2-D) [25].

Vartuli et al [27] have reported the formation of an additional molecular species, a cubic octamer  $[(CTMA)SiO_{2.5}]_8$  (see Table 1.1).

Table 1.1. Composition of the synthesis mixtures for the formation of various M41S phases [ref. 27]

Product	<sup>a</sup> Sur/Si molar ratio of gel	<sup>b</sup> TEOS/100 g of <sup>c</sup> CTMAOH
MCM-41	0.6	30 g
MCM-48	1.0	20 g
Lamellar	1.3	15 g
Cubic octamer	1.9	10 g

<sup>a</sup>Surfactant to silicon mol ratio

<sup>b</sup>Tetraethyl orthosilicate

<sup>c</sup>Cetyltrimethylammonium hydroxide

A highly ordered MCM-41 analogue, designated FSM-16, was discovered at about the same time as the M41S materials [28, 29]. Its synthesis involved ion exchanging the interlayer Na<sup>+</sup> ions of kanemite with CTAB. It has also recently been prepared by cetylpyridinium bromide templating of water glass [30].

### 1.2. Synthesis and Fabrication of Mesoporous MCM-41

The preparation methods of M41S materials are reminiscent of the synthesis of zeolites [31] in that they involve the hydrothermal transformation of alkaline silicate or aluminosilicate gels in the presence of a template. Unlike conventional zeolite synthesis, MCM-41 materials are prepared from a cationic surfactant template and silica polyanions through an electrostatic interaction (S<sup>+</sup> $\Gamma$ ). The main synthesis methods used to prepare the Mobil mesoporous materials thus far are liquid crystal templating and sol-gel processing. A summary and the background to these two methods is given below.

## 1.2.1 Liquid-Crystal Templating (LCT): Supramolecular Self-Assembly

Through charge matching between the hydrophilic head groups of surfactant molecules and inorganic precursors, silicates and surfactants can be self-assembled into supramolecular aggregates with long-range packing order [32 - 34]. Upon removal of surfactants through calcination or organic washes, mesoporous silicates with ordered porous arrays can be achieved.

A distinguishing feature of the M41S synthesis is that quaternary ammonium surfactants,  $C_nH_{2n+1}Me_3N^+$ , with different alkyl chain lengths (n = 8-18) are used as templates [25, 26]. Surfactants are large organic molecules [ $C_nH_{2n+1}(CH_3)_3N^+$ ] with a hydrophilic head group and a long hydrophobic tail of variable length, and are capable of forming micelles or liquid crystal phases in aqueous solutions at a critical micelle concentration (CMC). Researchers have termed the mechanism of formation of these mesoporous materials a LCT mechanism, (see Figure 1.2).



Fig. 1.2. Liquid-crystal templating (LCT) mechanism for self-assembly proposed by Beck et al [26] showing two possible pathways for the formation of MCM-41: (1) liquid-crystal initiated and (2) silicate-initiated.

Pathway 1 assumes that the primary structure-directing element is the water/surfactant liquid-crystal phase, whereas pathway 2 suggests that the addition of the silicate orders the subsequent silicate-encased surfactant micelles. The investigation of this system by Chen et al [35] revealed that the formation of the mesoporous structure occurs by the second mechanism, and does not follow a templating process by an initially ordered liquid-crystalline phase. A charge matching interaction between the hydrophilic head groups of surfactant molecules and inorganic precursors has also been proposed [32-34], in which silicates and surfactants can be self-assembled into supramolecular aggregates with long-range order of packing. In short, the highly ordered MCM-41 porous structure is not caused by single guest ions or molecules, but by a supramolecular self-assembly of surfactant molecules in aqueous solutions.

Subsequent research has shown that not only milder hydrothermal conditions give good quality Si-MCM-41 materials, but that materials can also be prepared at room temperature [36-38], under ultrasound radiation [39], as well as under microwave radiation [40, 41]. High Al-containing MCM-41 (Si/Al = 1.5) has also been prepared at room temperature [42]. The syntheses by ultrasound and microwave radiation were

efficient in yielding the best quality Si-MCM-41 over a relatively short time (3.5 and 4 h, respectively). Thus the usually longer crystallization times required for synthesizing advanced materials is significantly reduced.

This versatility in the conditions under which the MCM-41 materials can be synthesized, as opposed to the normal difficulties in synthesizing conventional microporous zeolites, makes them amenable to study in various fields.

## 1.2.2. Sol-Gel Synthesis Route (Alkali-free Synthesis)

Sol-gel chemistry originated in the mid-1800s with several studies on the creation of silicon dioxide (SiO<sub>2</sub>) glass from the tetraethoxysilane (TEOS) precursor [43, 44]. It has subsequently been defined as the preparation of a ceramic material (e.g. glass) by the preparation of a sol, gelation of the sol, and subsequent removal of the solvent [45 - 47]. Depending on the nature of the precursors, the sol-gel process can be classified into two different routes: a) inorganic route where the precursor is an aqueous solution of an inorganic salt (e.g. sodium silicate solution), or b) organic route where the precursor is a metal-organic compound (e.g. TEOS) [48]. Metal alkoxides or tetraalkoxysilanes are most commonly preferred as precursors, because: they are soluble in organic solvents (providing high homogeneity), they can easily be converted to the corresponding oxides, and they are known for almost all elements [49-51]. Metal oxides can be created from tetraalkoxysilanes via a two-step process shown below for the formation of SiO<sub>2</sub> from TEOS:

 $Si(OR)_4 + n H_2O \rightarrow Si(OH)_n(OR)_{4-n} + n ROH$ ,

where R is, for example, a  $-CH_2CH_3$  group. This step represents the nucleophilic substitution of the alkoxide groups with hydroxyl groups. The second step is a condensation process that initiates the silicate glass structure:

 $\equiv$ Si(OH) + RO-Si $\equiv \rightarrow \equiv$ Si-O-Si $\equiv$  + ROH, or

 $\equiv Si(OH) + HO-Si \equiv \rightarrow \equiv Si-O-Si \equiv + H_2O$ 

The condensation process continues to make an extended three-dimensional silicate glass matrix.

In general, the sol-gel procedure consists of the steps outlined below [52]:

- 1. Preparation of a homogeneous solution either by dissolution of a metal organic precursor (TMOS, TEOS, Zr(IV)-Propoxide, Ti(IV)-Butoxide, etc.) 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 containing either HCl, NaOH or NH<sub>4</sub>OH).
- 3. Aging: The sol changes into a gel by self-polymerization.
- 4. Shaping the gel to the finally desired form (thin films, fibres, spheres, etc.).
- Converting (sintering) the shaped gel to the desired ceramic material generally at temperatures around 500 °C.

Removal of the pore liquid under hypercritical conditions yields a network that does not collapse and results in the production of an aerogel [53]. When the pore liquid is removed by evaporation under normal conditions, shrinkage of the pores occurs and a xerogel is formed.

Over the years, the sol-gel chemistry approach has been developed into a powerful tool for making films and coatings, optics, fibres, powders, and membranes with desired characteristics [45, 54]. The potential benefits of sol-gel processing over the conventional powder route [45, 54, 55], include the following: (i) good homogeneity, (ii) ease of chemical composition control, (iii) high purity, (iv) low-temperature

processing, and (v) large area and versatile shaping over vacuum deposition techniques.

However, unless structure-directing materials are employed, the materials obtained in a simple sol-gel process are amorphous and randomly ordered [45]. Thus, the synthesis approach to ordered mesoporous silicate frameworks of the MCM-41 architecture, requires that a surfactant template be edded to the sol-gel mixture [56-59]. The sol-gel method has a great potential in making nanocomposite materials.

### 1.2.3. Other Mesoporous Materials: Post-LCT Syntheses

The novel structures and properties of MCM-type mesoporous molecular sieves, have prompted the extension of the ideas of liquid crystal templating used to synthesize the M41S silicates, to the synthesis of other silica and non-silica analogues [33, 60]. The organic/inorganic interface chemistry for the synthesis of these mesostructured surfactant-inorganic arrays involves four different interactive routes [33, 61]: (S<sup>+</sup>Γ), (S<sup>-</sup>Γ<sup>+</sup>), (S<sup>+</sup>X<sup>-</sup>Γ<sup>+</sup>) and (S<sup>-</sup>M<sup>+</sup>Γ), where S<sup>+</sup> = cationic surfactant, S<sup>-</sup> = anionic surfactant, I<sup>+</sup> = cationic inorganic species, Γ = anionic inorganic species, X<sup>-</sup> = (Cl<sup>-</sup>, Br<sup>-</sup>) and M<sup>+</sup> = (Na<sup>+</sup>, K<sup>+</sup>, etc.). Consequently, the synthesis involving these interactions has been referred to as the generalized or cooperative synthesis mechanism.

## 1.2.3.1. Silica-Based Mesoporous Materials

Ever since the disclosure of the M41S family of mesoporous materials in 1992, a veritable explosion of research effort has occurred in macromolecular and micelle templated syntheses of mesostructured materials. Consequently, many synthetic routes and strategies have been developed to yield a wide diversity of various frameworks with different chemical compositions and pore structures. The actual differences are due to the nature of the electrostatic interactions between the organic and inorganic phases. The initial Mobil silicate-based materials were prepared in a

process involving direct ionic bonding between the liquid-crystalline cationic surfactant assemblies and an anionic silicate species (S<sup>+</sup>I<sup>-</sup> interaction) [25, 26], giving rise to the so-called liquid-crystal templating (LCT) mechanism. Post-M41S advances have led to the development of synthesis models based on the interfacial interactions between the surfactant and the inorganic species, and also on the fact that the silicate species promote the formation of a liquid crystal phase below the critical micelle concentration (CMC). In addition to the previously mentioned  $(S^{+}\Gamma)$  pathway, the  $(S^{-}\Gamma)$  $I^{+}$ ) pathway has been developed [62] which involves the condensation of an anionic surfactant with cationic inorganic species. Two other routes were also developed in which the surfactant and the inorganic phase have similar charges, but are separated from each other by small ions with opposite charge:  $(S^{+}X^{-}I^{+})$  with  $(X^{-} = CI^{-}, Br^{-})$  and  $(S^{-}M^{+}\Gamma)$  with  $(M^{+} = Na^{+} \text{ or } K^{+})$  [33, 62]. At the same time, an elegant route was proposed by Tanev et al [63-65] to prepare mesoporous silicas at room temperature by a neutral templating route  $(S^0I^0)$ . In this case, the organic surfactant is not a quaternary ammonium cation but a primary amine (dodecylamine), and the selfassembly involves hydrogen-bonding interactions between the neutral primary amines and neutral inorganic precursors. The resulting materials, denoted HMS (hexagonal mesoporous silica), can be considered as special members of the M41S family, but differ significantly from the molecular sieves obtained by electrostatic assembly pathways. They usually possess thicker framework walls (2-3 nm compared to ca. 1 nm for MCM-41), smaller X-ray scattering domain sizes and a textural mesoporosity. The small X-ray scattering domain sizes, evidenced by the absence of narrow (110) and (200) reflections in the X-ray pattern, reflect a short range hexagonal order compared with MCM-41. One of the most important advantages of HMS compared with MCM-41 is that the organic phase (SDA) can be removed from the as-synthesized samples by solvent extraction, which is not possible in the case of other pathways where strong electrostatic interactions exist between the organic and inorganic phases [64]. The solvent extraction prevents the partial degradation of the mesoporous structure that could occur during calcination in air at relatively high temperatures. Hexagonal mesoporous silica (HMS), due to their thicker and more

condensed pore walls, are more hydrothermally stable than the materials prepared through cationic templating [66].

Other models describing the micelle-templated synthesis of mesoporous silica have been proposed. These include silicate rod assembly [67], silicate layer puckering [68], charge-density matching with the possibility of deriving MCM-41 from a lamellar phase [32], true liquid crystal templating [69], and cooperative templating (a.k.a. generalized LCT model) [33, 61]. A wide spectrum of novel structures have been obtained through these templating mechanisms.

The use of gemini surfactants of the form  $C_nH_{2n+1}N^+(CH_3)_2(CH_2)_sN^+(CH_3)_2C_mH_{2m+1}$  as templates at room temperature has produced mesoporous silica frameworks like SBA-2 (3-D hexagonal mesophase, space group P6<sub>3</sub>/*mmc*) [61], SBA-3 (similar to MCM-41) and SBA-1 (cubic, (*Pm3n*)) [33, 62], as well as MCM-48 [61]. However, the use of neutral gemini surfactants of the type  $C_nH_{2n+1}NH(CH_2)_2NH_2$  gave rise to MSU-G mesoporous silica from TEOS [70].

SBA-2 synthesized at room temperature in alkaline pH with the gemini surfactant  $[CH_3(CH_2)_{15}N(CH_3)_2(CH_2)_3N(CH_3)_3]^{2+}$  has been found to adopt a number of morphologies [71], including hollow spheres (*ca.* 100 µm diameter), flat plates (50 µm across), and small spheres (1-2 µm diameter). As seen in Figure 1.3 below, the plates appear to be formed directly by rupturing the hollow spheres:



Figure 1.3. SEM micrograph of SBA-2 showing different morphologies [ref. 71]

An ordered mesoporous silica with a novel cubic structure (space group Fd3m) has been synthesized by using tri-head group quaternary ammonium surfactants as the structure-directing agents under basic conditions at low temperatures [72]. Tri-head group surfactant amphiphiles are a kind of multicharge cationic surfactant with three head groups separated by different methylene chains and a variable length hydrophobic tail, and are closely related to gemini surfactants [34, 73, 74]. The higher charge in the former type of surfactants enables it to interact strongly with water molecules and to easily give new amphiphile self-aggregation [75]. The resulting mesoporous materials have uniform nanopore size (~3.0 nm) and large surface areas (~960 m<sup>2</sup>/g).

A number of neutral templating methods used to synthesize mesoporous silicas, such as the use of polyethers, have been reported in the literature [64, 65, 76-78]. The templating mechanism in this case is presumed to involve a phase separation of the hydrophobic and the hydrophilic part of the long chain polyethylene molecules prior to the formation of the molecular sieves. A prototype of a mesoporous silica obtained via this route is SBA-15, with periodic pores of dimensions in the range 50-300 Å, and synthesized using an amphiphilic tri-block copolymer,  $[EO_{20}-PO_{70}-EO_{20}]$  as

organic SDA in aqueous acidic medium [76, 77]. Further developments in the triblock copolymer-templated syntheses have also given rise to FDU-1, a cubic (*Fm3m* structure) mesoporous silica with a 3-D hexagonal channel system [79, 80]. The template used in this synthesis is a tri-block copolymer ( $EO_{39}BO_{47}EO_{39}$ ) and TEOS serves as a silica source. A related type of nonionic surfactant-templated synthesis of mesoporous silica uses Vitamin E TPGS as structure-directing template [81]. The resulting mesoporous silica referred to as DAM-1, has a highly ordered, hydrothermally-stable, 2-D hexagonal mesostructure with various morphologies being achieved, including spheres, gyroids, discoids, hexagonal plates and rods.

A novel mesoporous silica molecular sieve (designated KSW-2) is also obtainable from mild acid treatment of a layered alkyltrimethylammonium ( $C_nTMA$ )-kanemite complex [82, 83]. This material is different from the hexagonal mesoporous silica (FSM-16) derived from kanemite [29, 84] in that it has an orthorhombic structure with rectangular arrangements of semi-squared one-dimensional channels. A 3-D cubic mesoporous structure, SBA-12, has also been synthesized using the oligomeric alkyl-ethylene oxide surfactant, Brij 76 ( $C_{18}EO_{10}$ ) [77].

Although the mesoporous silica material MSU-X was prepared by a neutral surfactant assembly pathway using TEOS and nonionic surfactants [65], a related mesoporous silica molecular sieve, with a wormhole-like framework typical of MSU, was obtained under acidic conditions using a low-cost and biodegradable amphoteric surfactant template, tetradecyl betaine [85].

Inexpensive non-surfactant templates, e.g. triethanolamine (TEA), have been found to direct the synthesis of well-defined, hydrothermally-stable mesoporous siliceous oxides, denoted TUD-1 [86]. The mesopore size distribution of these mesoporous materials can be controlled by altering the reactant composition and the preparation variables [87]. Their pore sizes can be tuned in the range 25-250 Å and the surface areas varied between 400 and 1000 m<sup>2</sup>/g.

### 1.2.3.2. Metal Oxide-Based Mesoporous Materials

The "generalized liquid crystal templating" mechanism, also known as "cooperative templating model", [33, 61] can be extended to non-silica mesostructured materials synthesis. This method is based on the specific type of electrostatic interaction between a given inorganic precursor and surfactant head group. So far, this cooperative model has been regarded as the most plausible mechanism for the formation of mesoporous materials. Following this approach, a number of mesoporous metal oxides such as antimony oxide and tungsten oxide have been synthesized [33, 62]. Other research groups have also reported the templated syntheses of mesoporous metal oxides and representatives include: alumina [62, 88-90], titania [91, 92], vanadium oxide [93, 94], zirconia [95-98] and zirconium oxophosphate [99, 100], hafnium oxide [101], manganese oxide [102], iron oxide [103] and iron sulfides [104].

Ying and his group have developed an approach called "ligand-assisted templating" (LAT) to ensure a proper precursor-template interaction and micellar self-assembly prior to precursor hydrolysis [105, 106]. In the ligand-assisted templating approach the inorganic components (alkoxides) are covalently bonded to the long-chain amine template before the hydrolysis and condensation of the precursor. This approach allows the selective hydrolysis and condensation of the oxide precursor on the micellar surface and prevents the uncontrolled precipitation of particulate oxide materials that is commonly observed in non-silicate materials. Meanwhile, Ying and coworkers have used the "ligand-assisted templating" mechanism to form non-silica based metal oxides using amine surfactants. This synthesis approach resulted in the preparation of a new family of hexagonally packed mesoporous transition metal oxides termed TMS1 [91,105-109], based mainly on niobium oxide, for example, Nb-TMS1, a niobium oxide analogue of the hexagonally packed mesoporous silicate-based MCM-41 was prepared using this approach. Tantalum oxide molecular sieves were also obtained by this templating approach [107].

Other approaches, including the use of amphoteric surfactants for preparing mesoporous zirconia [110], have also been reported.

# 1.2.3.3. Carbon-Based Mesoporous Materials

Most work in the field of carbon-based mesoporous materials has been carried out by Ryoo's group at KAIST (Korea Advanced Institute of Science and Technology). The resulting materials are designated CMK-n, where CMK is an acronym for Carbon Mesostructures at KAIST:

CMK-1 was the first member of the ordered mesoporous carbon molecular sieves to be synthesized [111]. It was prepared by using MCM-48 mesoporous silica molecular sieves as template and sucrose as the carbon source. Substitution of the MCM-48 template with SBA-15 gave rise to CMK-3 [112], which shows retention of the template structural symmetry (*See Figure 1.4*):



Fig. 1.4. (Left): Changes in powder XRD patterns during synthesis of the carbon molecular sieve CMK-1 with its silica template MCM-48: (a) The mesoporous silica molecular sieve MCM-48, (b) MCM-48 after completing carbonization within pores, and (c) CMK-1 [ref. 111]. (Right): Powder XRD patterns of CMK-3 carbon and SBA-15 silica used as template for the CMK-3 synthesis [ref. 112].

After removal of the template (silica framework) using an aqueous solution of sodium hydroxide or HF, the mesoporous carbon structure was obtained. The XRD patterns of both CMK-1 and CMK-3 showed no peaks in the region  $2\theta > 10^{\circ}$ , indicating that the carbon framework was atomically disordered. These properties coupled with the high specific surface area (BET area 1380 m<sup>2</sup>/g and 1520 m<sup>2</sup>/g, respectively) suggest that the carbon molecular sieves can be useful as catalytic materials in hydrophobic applications and as adsorbents for the removal of organic pollutants, as well as in organic-sampling applications. Importantly, Kang et al [113] have recently reported

the regeneration of highly ordered mesoporous silica from CMK-3, which showed the reversible replication between carbon and inorganic materials.

By analogy with the synthesis of CMK-1 above, a mesoprous carbon molecular sieve was formed using UTD-1 as structure directing template [114], which was found to have an 'inverse' TUD-1 structure, with surface area  $> 1000 \text{ m}^2/\text{g}$  and tunable mesopore size.

## 1.2.4. Methods of Template Removal from the Mesostructure

The surfactant structure-directing agent (SDA) used to organize the silicate oligomers during preparation is usually trapped inside the solid inorganic matrix, forming a cast of the ordered nanoscale structure. Thus, the method by which it is removed is critical in obtaining the final mesoporous molecular sieves, as it can alter the structure and the porosity of the material. By far the most common method of removing the SDA (by analogy with microporous zeolites synthesis) after material synthesis is calcination. In this process the material is heated slowly in an oxidizing environment, that converts the organic species into gaseous oxides. In addition to this conventional method, used in the initial reports on the synthesis of MCM-41, various other relatively new methods for removing the occluded surfactant template from the pores of the resulting mesophase have been reported:

(a) Sample controlled thermal analysis (SCTA) [115], has been successfully used [116] to remove the template from as-synthesized Si-MCM-41. This technique also allowed a study of the mechanism of thermal degradation of the cationic surfactant CTAB occluded in a pure silica MCM-41-type material, as well as the consequences on the porous properties of the final material.

(b) Solvent extraction of the surfactant template using ethanol solutions of acids or salts [66,117-120]. Advances in the solvent extraction of the template after MCM-41

synthesis led to supercritical fluid extraction (SFE), reported by Kawi and Lai [121]. This method allows the surfactant template to be recovered and re-used.

(c) Extraction by ozone treatment [122, 123] of the as-prepared MCM-41 mesostructure in its mother liquor results in mesoporous MCM-41 with larger pores than the similar material prepared by traditional calcination.

(d) Silylation with ethanolic solutions of alkylsilanes and alkylsiloxanes [124], was found to achieve simultaneous template extraction and direct surface modification.

(e) Treatment of uncalcined MCM-41 with trialkylchlorosilanes [125] has also been identified as a method for template removal after MCM-41 synthesis.

Template removal is typically achieved by either calcination or solvent extraction or a combination of the two methods.

## 1.3. Characteristics of Mesoporous Materials (MCM-41)

### 1.3.1. Bulk and Textural features of MCM-41

Mesoporous MCM-41 materials are characterized by exceptionally high specific surface areas ( $\geq 1000 \text{ m}^2/\text{g}$ ), high thermal stability and a narrow monodisperse pore size distribution. Other attractive properties of MCM-41 materials are high hydro-carbon sorption capacities (> 50 wt% cyclohexane at 40 torr, 49 wt% *n*-hexane at 40 torr, and 67 wt% benzene at 50 torr) and pore volumes in the range 0.7-1.2 cm<sup>3</sup>/g. MCM-41 consists of a honeycomb structure that results from a regular hexagonal array of uniform unidimensional cylindrical pores. The initial results from the Mobil researchers [25, 26, 64] showed that it is possible to tailor the pore sizes of these materials to be in the range 20-100 Å, by both manipulating the alkyl chain length of the cationic surfactant template used in the synthesis and by adding auxiliary hydro-

carbons, such as mesitylene to the synthesis mixture. Materials with pore sizes greater than 40 Å, and up to 100 Å, could be synthesized using reaction mixtures containing auxiliary organics (mesitylene). The pore structure of the resulting materials, as seen under transmission electron microscopy (TEM), is depicted in Figure 1.5:



Fig. 1.5. TEM images of MCM-41 materials with Ar pore sizes of (a) 20, (b) 40, (c) 65, and (d) 100 Å. [ref. 26]

From Figure 1.5 above, it is apparent that all samples show the hexagonal structure, although smaller pore size materials (< 40 Å) show the most regular hexagonal arrangement of uniform pores, i.e. those prepared in the absence of any organics. The regularity decreases as the pore size increases.

In contrast to the addition of auxiliary organics to swell the pore diameters of MCM-41, Corma et al [126] were able to prepare swollen, highly ordered MCM-41-type materials by adjusting the CTMA/SiO<sub>2</sub> ratio of the synthesis gel in the range 0.09 to 0.15 and by carrying out the synthesis under hydrothermal conditions.

A typical XRD pattern of MCM-41, together with a nitrogen adsorption isotherm are shown in Figure 1.6 below. The powder XRD pattern shows three to five Bragg peaks in the region  $2^{\circ} < 2\theta < 10^{\circ}$ , indicating the long-range order present in this material. Since the reflections are due to the ordered hexagonal array of parallel silica tubes, they can be indexed assuming a hexagonal unit cell as (100), (110), (200), (210) and (300). A useful parameter is the lattice constant or repeat distance (a<sub>o</sub>) between two pore centres. This may be calculated by  $a_{o} = 2d_{100}/\sqrt{3}$ , where  $d_{100}$  is the interplanar spacing corresponding to the (100) Bragg reflection. For the material whose interplanar spacing  $d_{100}$  is about 40 Å, the lattice parameter  $a_{o}$  is about 45 Å.



Fig. 1.6. XRD pattern (a) of high-quality calcined MCM-41 reported by Huo et al [34], and  $N_2$  adsorption isotherm (b) reported by Branton et al [127].

The adsorption isotherm (Figure 1.6b) gives information on the predominant type of pores in the MCM-41 material. It corresponds to a reversible type IV isotherm, indicating the presence of mesopores. A sharp increase in the adsorbed and desorbed volumes at a relative pressure  $P/P_o \sim 0.42$  reflects the uniformity of the pore-size

distribution, and corresponds to capillary condensation in the mesopores. The average pore diameter in this sample, calculated using the Barrett-Joyner-Halenda (BJH) method, was very narrow at 3.3 nm.

## 1.3.2. Morphologies and Shapes in Mesoporous MCM-41 Materials

Controlling the macroscopic morphology of mesoporous materials could generate potential practical applications for these systems. Therefore, there has been a great deal of work performed on the development of mesoporous MCM-41-type materials with controlled morphologies and shapes such as films [128-132], fibres [130-135], spheres [136-140], monoliths [69, 141, 142], ropes and gyroids [143], etc.

Si-MCM-41 can also be prepared such that a bimodal distribution of morphologies is observed [144, 145]. Figure 1.7 below shows the bimodal morphologies of MCM-41 reported by Schulz-Ekloff et al [144], consisting of both worm-shaped and spherical MCM-41 particles and called bimodal silica (BMS):



Fig. 1.7. SEM images of (a) BMS-1, (b) BMS-2, and (c) BMS-3. The length of the bar for (a, b) corresponds to 5  $\mu$ m and for (c) corresponds to 10  $\mu$ m. Varying amounts of ethyl acetate were added to the synthesis mixture for the preparation of the BMS materials, with BMS-1,

BMS-2 and BMS-3 prepared by adding 15, 25 and 35 ml, respectively, of ethyl acetate to the synthesis gel. [ref. 144]

The above distribution has been achieved by homogeneous precipitation from an isotropic reaction mixture, wherein the hydrolysis of ethyl acetate led to a decrease in the pH of the reaction mixture and consequent formation of solid particles.

A critical property of MCM-41 materials, which has a direct bearing on their practical utility, is the hydrothermal stability in reactions that produce water as a by-product. Section 1.3.3 is dedicated to the origin of this property and ways or methods through which it can be circumvented.

### 1.3.3. Hydrothermal Stability of MCM-41 Materials

While MCM-41 has been reported to have high thermal stability in air, O<sub>2</sub> and water vapour [119, 146, 147] it has low hydrothermal stability in boiling water and aqueous solutions. This poor hydrothermal stability is the limiting factor in the potential application of these materials to several types of hydrocarbon processing procedures and adsorption processes requiring heavy-duty regeneration. The origins of this poor stability is related to their thin pore walls of *ca*. 5 Å [25, 148], which are also amorphous [100], and can be easily destroyed by hydrolysis of the Si-O-Al or Si-O-Si bonds. Dealumination can also occur during calcination. The laws of sintering state that the existence of a small hole between parallel pores creates a highly unstable situation in aluminosilicates and silicates [45], and since MCM-41 materials possess such pores, dealumination should lead to unstable materials. Other groups have proposed that the loss of structure in MCM-41-type materials under hydrothermal conditions involves silicate hydrolysis by water adsorbed onto the silanol groups [149, 150]. It has also been found that mesoporous silicates undergo a temperatureinduced phase transformation during synthesis [151], resulting for example, in MCM-48 being easily and rapidly (less than 6 h) produced from MCM-41. Thus, control of the temperature is also an important factor in producing MCM-41 under hydrothermal conditions. Enormous efforts have been made to improve the stability of these mesoporous materials either by changing the synthesis procedure or by modifying the materials after synthesis, and a review of the several methods advanced in this regard are given in the next section.

## 1.3.3.1. Improving the thermal/hydrothermal stability of Si-MCM-41

The structural stability of MCM-41 samples in boiling water can be improved by changing synthesis variables such as the hydrothermal synthesis temperature [152], alkyl chain length of the templates [152], type of silica source [153], pH during synthesis [146, 154-156], as well as inorganic and organic salt addition (sodium chloride, sodium acetate, sodium fluoride, tetraalkylammonium ions, EDTA) during the crystallization process of the pure silica material [146, 158-163]. A combination of repeated pH adjustments during synthesis and the salt effect [164, 155] has been found to significantly enhance the hydrothermal stability of the resulting pure silica MCM-41.

Several approaches have also been proposed that include enhancement of the condensation of the silanol groups by replacing NaOH with small alkylamines as mineralization [165], preparation of materials with thicker pore walls by controlling the synthesis gel composition (the OH<sup>-</sup>/SiO<sub>2</sub> ratio) [76, 166] or by secondary synthesis using Si-MCM-41 as a silica source in a two-step synthetic process over long crystallization times [167, 168], inclusion of fluoride ions in the synthesis gel for MCM-41 or SBA-15 [162, 169-173], one-step organic modification [174] and post-synthesis hydrothermal restructuring in water [175, 176]. Incorporation of elements such as titanium or aluminium into the walls [177 - 180], or even ion exchanging calcined AlMCM-41 with Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Y<sup>3+</sup> [146] has been found to improve the hydrothermal stability of the MCM-41. Several other post-synthesis treatments have been shown to improve the hydrothermal stability of siliceous MCM-41. These include grafting of Al onto Si-MCM-41 materials [181] or incorporating Al into Si-MCM-41 [182, 183], treatment with acid [120, 184], coating of pore interiors with further layers of silica [185, 150] or alumina [186], dispersion of a ZrO<sub>2</sub> monolayer on MCM-41 [187] and surface modification of MCM-41 with Grignard reagents [188, 189]. The latter approach gives stable Si-C bonds that render the material highly hydrophobic and consequently hydrothermally stable. Other effective modifications are the complete [150, 190, 191] or partial [192] hydrophobization of the surface by trimethylsilylation to preclude water attack. However, Pan et al [193] found that the BET surface area and pore size of the MCM-48 silylated by trimethyl chlorosilane (TMCS) decreased markedly, hence retarding the advantages of MCM mesoporous materials possessing high surface areas and big pore sizes.

A unique method for addressing the hydrothermal instability of mesoporous materials was reported by Galarneau et al [194]. The method involves using intercalated surfactants in the interlayer spaces of smectite clays to template the polycondensation of TEOS, resulting in materials with thermally stable mesopores, referred to as porous clay heterostructures (PHCs).

The importance of Al incorporation has been emphasized by the results of Kawi and Chen [195], who found that substitution of Al in the material framework or by introduction of non-structural Al species onto the pore surface of MCM-41 has the effect of stabilizing the mesoporous framework of the resulting materials in boiling water. This is indicated by the XRD patterns (Figure 1.8) and BET surface analysis data (Figure 1.9).



Fig. 1.8. Powder XRD patterns of Si-MCM-41 and Si-Al-MCM-41 (a) before and (b) after treatment in boiling water for 1 week [ref. 195]



Fig. 1.9.  $S_{BET}$  of Si-MCM-41, Si-Al-MCM-41, and Al/Si-MCM-41 before and after treatment in boiling water for 1 week: • fresh sample,  $\Box$  in boiling water. The last material was prepared by Al impregnation of Si-MCM-41. [ref. 195].

It can be seen from the data above that Si-MCM-41 loses most of its surface area (from 1301 to 107  $m^2/g$ ) after it had been soaked in boiling water for 1 week, whereas Si-Al-MCM-41 still maintains its surface area around 1000  $m^2/g$  under treatment in boiling water for 1 week. In contrast to these observations, He et al [196, 197] reported that Al(III) decreased the thermal and hydrothermal stability of MCM-41 materials, whereas La(III) and Fe(III) improved these properties.

Recent advances in the synthesis of MCM-41 materials with thickened pore walls have led to the use of high-pressurized (12 MPa) synthesis conditions [198], decreasing the pore diameter of the template micelles [199], and increasing the hydrothermal synthesis time and temperature [200].

## 1.4. Catalysis and Technical Applications of MCM-41 Materials

Si-MCM-41 mesoporous materials lack intrinsic catalytic applicability by themselves, but can be modified with organic functional groups or heterogenized with transition metals in order to make them suitable for various applications. Work in these two fields is briefly reviewed in the next subsections. In the metal-containing variants of MCM-41, Fe and Co-derivatized materials will be discussed separately from the other metallated species, because such materials form part of thesis study. The catalytic applications of the rest of the metal-variants of MCM-41 will be described in section 1.4.3.

### 1.4.1. Organically-Modified MCM-41 Materials

Many applications (such as adsorption, ion exchange, catalysis and sensing) require mesoporous materials to have certain attributes such as binding sites, stereochemical configuration, charge density and acidity [201-203]. Therefore, by analogy with the chemistry of organically-modified silicates or ORMOSILs [204-206], MCM-41-type

materials can also be modified by attachment of organic functionalities to their surfaces in order to increase their potential applicability, an aspect that forms an important research area in heterogeneous catalysis and green chemistry [207]. The interest in inorganic-organic hybrid materials arises from the advantages that the inorganic and organic moieties bring to the systems [208, 209], viz., that the inorganic components can provide mechanical, thermal or structural stability, while the organic features are often more readily modified for specific applications in catalysis, separation, or sensing [210]. The typical precursors in the preparation of inorganic-organic hybrid materials are organically functionalized metal alkoxides, whose Si-C bonds should be hydrolytically stable under acid or base conditions. The ordered mesoscopic inorganic-organic hybrid materials contain easily modifiable organic functional groups for applications as catalysts, catalyst supports, and stationary phases in chromatography which take advantage of the high surface areas and specific size selectivities of the mesoporous silicate structures [211].

Since the discovery of MCM-41, its organically-modified derivatives have also been prepared by either post-synthesis grafting or co-condensation of tetra-alkoxysiloxane and one or more organo-alkoxysilanes through the sol-gel process [212, 213]. The organic functionalization of silicates has been found to play an important role of permitting precise control over the surface properties, modification of the hydrophilic or hydrophobic character of the surface, alteration of the surface reactivity, protection of the surface from attack, modification of the bulk properties of the materials and at the same time stabilizing the materials towards hydrolysis [209, 214-217].

Representative catalytic reactions catalyzed by organically-modified mesoporous silica are described in this section, separate from those of the Fe- or Co-MCM-41 materials and those of other derivatives of the M41S materials. Both direct and post-synthesis methods are used in their preparation as outlined below.

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### 1.4.1.1. Co-condensation or Direct Organic Modification of MCM-41

Co-condensation of the reactive species during the mesopore synthesis is a method to incorporate functionality into the walls of a channel system [218]. This approach is an extension of the organically-modified sol-gel derived materials. The co-condensation method is the most common and direct synthesis route to the introduction of organic groups into a silica network [219-221], and provides better control over the amount of organic groups incorporated into the matrix and ensures the uniform surface coverage with organic groups under mild conditions. The preparation method involves co-condensation of TEOS and organosiloxanes in the presence of surfactant templates at room temperature, giving rise to covalently linked, ordered, hybrid inorganic-organic networks. The role of TEOS is to act as a primary silica source and as reagent for the formation of fully saturated Q<sup>4</sup> linkages which are required to maintain structural integrity in the organo-silica-surfactant mesophases [222].

Although many research groups have synthesized organically-modified mesoporous silicates through this method [211, 222-226], of particular interest is the work of Macquarrie [227, 228], who showed that functionalizing MCM-41 with aminopropyl functional groups by a one-pot method gives rise to an effective Knoevenagel condensation catalyst. Direct organic modification of Ti-MCM-41 materials has been found to produce highly efficient catalysts for epoxidation reactions [229-231].

## 1.4.1.2. Post-synthesis Organic Modification of MCM-41

In the post-synthesis grafting method, the surface of the pre-fabricated inorganic mesoporous materials (MCM-41 has a high density of surface silanols) is reacted in a suitable solvent with organosilane coupling reagents through the surface silanol groups. This method has the advantage that the original structure of the mesoporous matrix is usually maintained intact. Post-synthesis grafting techniques have been used for many years to attach organic functionalities to mesoporous silicate surfaces [232],

making this a relatively older method when compared to the co-condensation in mesopores.

Through the grafting technique, [233] micelle-templated silicas (MTS) were functionalized with primary or secondary amine functions to achieve effective catalysts for the Knoevenagel condensation reaction. Quaternary tetraalkylammonium hydroxidegrafted MCM-41 was also found to be a strong Bronsted base catalyst [234] and an excellent alternative to homogeneous catalysts for Knoevenagel condensations, Michael additions and aldol condensations because of their high catalytic activity and good selectivity under mild conditions. Post-synthesis double organic modification [235] of Si-MCM-41 and Ti-MCM-41 using 3-chloropropyl and methyl groups produced efficient catalysts for the epoxidation of cyclododecene.

### 1.4.1.3. Decontamination of Ground Water: Heavy Metals and Oxyanions

Heavy metals, particularly mercury and lead, are important environmental pollutants, threatening the health of human populations and natural ecosystems alike. Removal of these species from the environment by selective binding on solid adsorbent surfaces is a major focus of waste treatment and cleanup efforts. The high surface areas combined with large and accessible pores of ordered mesoporous silicas (OMS) of the M41S family, make them good candidates for the creation of novel adsorbents of tailored surface properties for environmental applications [216, 236]. This tailoring can be achieved by post-synthesis coating of the inside surfaces of mesopores with an organic monolayer whose molecules are covalently bound to the silica. The free ends of the tethered molecules can be chemically tailored to sequester particular species from solution.

The adsorption of toxic metal cations has been explored for functional groups fixed on mesoporous silica. The divalent cations (Cu, Zn, Cr and Ni) present in waste-water are adsorbed to a greater extent on amino-functionalized SBA-15 than on thiolfunctionalized SBA-15, whereas  $Hg^{2+}$  is preferably adsorbed on thiol-functionalized SBA-15 [237]. The mercury adsorption on thiol-functionalized mesoporous silicas has been intensively studied [216, 236, 238-240]. Mercier and Pinnavaia's thiolfunctionalized mesoporous material, denoted MP-HMS [216], exhibited Hg(II) binding with sufficient efficiency to meet federal drinking water standards, along with an unprecedented loading capacity of 310 mg/g). Concurrent with this report, on thiol-functionalized HMS silica, Feng et al [236] reported an analogous heavy metal ion adsorbent based on the mercaptopropylsilyl functionalization of a calcined form of mesoporous MCM-41 silica. Although their grafting approach was similar to that reported previously for the functionalization of MCM-41 [241, 242], a much higher concentration of immobilized ligand was achieved through the use of a larger pore framework (5.5 nm) and a functionalization process that involved repeated surface hydrolysis and silvlation cycles. The mercury loading (505 mg/g) was even higher than that observed for functionalized HMS. This study showed that the formation of almost a monolayer of Si-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-SH was followed by bridging by Hg-O-Hg units to sulphur atoms, which earned these materials the codename FMMS (functionalized monolayers on mesoporous supports) and eventually SAMMS (selfassembled monolayers on mesoporous supports). An advantage of this type of strategy is that the adsorption site has a molecular nature so that the adsorption capacity can be estimated on the basis of stoichiometry. However, it was demonstrated that the ratio of Hg to S depended on the kind of mesoporous silica used [238].

Over the years, the FMMS or SAMMS technology has been developed at the Pacific Northwest National Laboratory (PNNL) in the USA), since these materials are extremely efficient in removing mercury, heavy metals, radionuclides and anions from both aqueous and nonaqueous streams. They can adsorb metals 30 to 10,000 times more effectively than current commercial filters, as the thiol groups of TMMPS-coated silica bind strongly to heavy metal ions (e.g.  $Hg^{2+}$  and  $Ag^{+}$ ). The adsorptive power of the material is measured in terms of the distribution coefficient, K<sub>d</sub>. The functionalized monolayers have shown a K<sub>d</sub> as high as  $10^{8}$  for mercury,

compared to  $10^4$  for other resin materials [243]. The stability and potential to regenerate and reuse these materials has also been demonstrated. A schematic summary of the synthesis of the silica sponge (SAMMS) and its final structure [236, 244, 245] is depicted in the figure below:



Fig. 1.10. Recipe for the formation of a silica sponge (A), and retention of the hexagonal structure B (ref. 245).

Studies on the nature of the interface chemical interaction between mesoporous silica and the substrate [246] have revealed that high-quality, close-packed monolayers can be formed on the nanoporous supports through the introduction of several layers of physically adsorbed waters on the nanoporous surface. The role of this physisorbed water is to physically confine all the hydrolysis and condensation reactions of the organosilanes to the interface. Figure 1.11 (a) and (b) below show direct chemical bonding between heavy metals and alkyl thiols for heavy-metal adsorption:



Fig. 1.11. Heavy metal removal by SAMMS [ref 246]

In summary, the SAMMS technology utilizes the unique properties of mesoporous materials (surface areas  $\sim 1000 \text{ m}^2/\text{g}$  and uniform pore size ranging from 1-50 nm) to functionalize up to 100 percent of the available surface area using self-assembly techniques. This results in a highly selective material with exceptional material loading and kinetic properties.

Numerous reports on the syntheses of metal-coordinated functionalized mesoporous silicas [218, 247-252] indicate how the structure of the adsorption site can capture cations (or anions).

The risk of exposure to toxic oxyanions in ground water is a rising environmental problem worldwide. These anions include arsenate and chromate that are particularly hazardous. The EPA maximum contaminant level for As in drinking water is 10  $\mu$ g/dm<sup>3</sup>, and naturally occurring excessive arsenic has been widely detected in wells in the Chikugo plain, Japan [253]. Under a range of conditions, arsenic and other

environmentally toxic metals such as chromium, exist in nature as tetrahedral oxyanions. Because efficient adsorption of target ions is not expected on the neutral silica surfaces of MCM-41 and other mesoporous silicas, the strategy of functional-ization of the surface must be designed for oxyanion adsorption. The high density of silanol groups (from 0.5 to 3.0 OH per nm<sup>2</sup>) [118] helps to fix large amounts of silanes with an adsorption activity onto a silica surface.

Unlike cation capture by amino- or thiol-functionalized groups, the studies of anion adsorption by functional groups fixed in the pores of mesoporous silicas are rare. Fryxell et al [254] have shown that diamino-functionalized MCM-41 exhibits a marked capacity for adsorption of  $Cu^{2+}$ , giving rise to a positively charged mesoporous host, which achieves nearly complete removal of arsenate and chromate by selective binding of the anions. The leaching of  $Cu^{2+}$  during the adsorption was not significant because of the affinity of the ethylenediamine ligand. In a related study on the adsorption of chromate and arsenate by amino-functionalized MCM-41 and SBA-1, Yoshitake et al [255] found that triaminosilane-grafted mesoporous silicas. Fe centres in functionalized mesoporous silica have been found to be environmentally benign and can readily remove pollutant oxyanions from waste water [256].

Another technical application of MCM-41 is based on the fact that SiO<sub>2</sub>-based mesoporous materials are suitable as host materials for semiconductors, due to their high degree of order as well as the large band gap of the SiO<sub>2</sub> (which serves as a barrier material). Several semiconductor compounds have been implanted into the MCM-41 silica to obtain regular arrays for quantum wires, e.g. CdS [257], CdSe [258], GaAs [259], InP [260], Ge [261] and SiGe [262]. In this light, Chen et al [263] reported the first successful incorporation of the semimagnetic semiconductor Cd<sub>1</sub>. <sub>x</sub>Mn<sub>x</sub>S into MCM-41 SiO<sub>2</sub>, as an alternative way of creating highly ordered arrays of magnetic quantum wires for possible applications in magneto-electronics. In other developments, 'ship-in-a-bottle' synthesis has been used in the preparation of tailored

metal structures in mesoporous silica like nanowires, which are interesting because of their novel electronic, optical and catalytic properties [264, 213]. Examples of metal nanowires prepared in mesoporous silica matrices are Cu [265], Pt and Rh [266, 267], Au [268], Bi<sub>2</sub>Te<sub>3</sub> [269], etc. Conducting filaments of polyaniline have also been prepared in a mesoporous channel host [270], and their a.c. conductivity has been demonstrated.

## 1.4.2. Metal-containing Mesoporous Materials (Me-MCM-41)

The incorporation of transition metals into microporous and mesoporous materials has drawn considerable interest because it results in materials with acid and/or redox properties [271-274]. However, the resulting redox molecular sieves need to be stabilized against leaching of the active metal component if they are to be used in liquid-phase reactions like the oxidation of alkenes, alkanes and alcohols with  $H_2O_2$ as oxidant [273]. Due to the special pore structure of M41S materials, they can be used as a matrix to immobilize catalytically active species onto or within the silica walls or as a host to accommodate certain guest compounds. Indeed, MCM-41 and MCM-48 are very widely studied members of this family, both as such and when they are substituted with redox metals such as Ti and V [275]. Metals across the periodic table have been incorporated into mesoporous M41S materials for various applications, and both their preparation methods and catalytic applications can be found in review articles such as [100, 276, 277]. Since this thesis will concentrate mainly on the chemistry of Fe- and Co-MCM-41 composite materials, with particular emphasis on their synthesis, characterization and applications, discussion will thus be restricted to these metals.

Several approaches have been used to incorporate transition metals into mesoporous MCM-41-type materials. These include direct [278-280], ion exchange [281] and template ion exchange (TIE) [282, 283], impregnation [284-286], metallocene

grafting [287 - 290], immobilization (Si-MCM-41s) [291] and ship-in-a-bottle (SIB) synthesis [292-298].

TIE as a preparation technique of metal ion-planted MCM-41 [282] has the advantage that metal loadings in the range Si/Metal = 20-320 can be achieved without collapse of the mesoporous structure. The technique is beginning to gain popularity in hetero-geneous catalysis.

### 1.4.2.1. Iron-containing Mesoporous MCM-41 (Fe-MCM-41)

Ferrisilicates are an important branch of iron-containing materials that catalyze a wide variety of reactions, ranging from acid-catalyzed processes to dehydrogenation and oxidation, e.g. oxidation of benzene to phenol by H<sub>2</sub>O<sub>2</sub> using a sol-gel-derived Fe/amorphous silica catalyst [299] and selective oxidation of benzene to phenol with N<sub>2</sub>O using Fe-ZSM-5 [300]. Metal-containing MCM-41, which possesses uniform nano-order mesopores and high concentrations of isolated active sites, has attracted much attention as a new type of oxidation catalyst, especially in liquid-phase oxidation reactions since facile diffusion of relatively large molecules can be expected.

The first direct synthesis of the Fe-MCM-41 was reported by Yuan et al [301]. This was a hydrothermal type of synthesis in which ferric nitrate was part of the initial synthesis gel mixture, although He et al [302] reported the first synthesis of similar materials at room temperature. Since then a number of reports have appeared on the synthesis and characterization of Fe-MCM-41 using different methods, including encapsulation of Fe<sub>2</sub>O<sub>3</sub> nanoparticles [303-306], wet impregnation [307], template ion exchange [308, 309], incipient wetness impregnation [310, 311], etc. However, all the iron-containing mesoporous silica materials prepared by direct synthesis with Fe(III) forming part of the synthesis gel, contained  $\leq 1$  wt% Fe. Remarkably, Pasqua et al [312] were able to control the incorporation of Fe to a loading of up to 5 wt%. This was achieved by incorporating the Fe precursor in the presence of the F<sup>-</sup> ions in

the synthesis gel at a neutral pH, giving materials with iron exclusively in the silicate lattice. At such a pH, stable mesoporous materials with thick silica walls with the iron loading up to 5 % were formed.

Furthermore, FeMCM-41 prepared under hydrothermal conditions showed evidence for the encapsulation as well as isomorphous substitution of trivalent iron in the MCM-41 [313].

Characterization of the Fe(III) environment in MCM-41 is important in accounting for the observed properties of the resulting materials. In zeolites, the Fe<sup>3+</sup> can occupy tetrahedral framework positions or octahedral extraframework positions [314]. Iron(III) has five d electrons and in aqueous solutions it forms mainly octahedral complexes. With weakly coordinating anionic ligands (like H<sub>2</sub>O, OH<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, etc.), as is the case in zeolite environments, it forms high-spin complexes with magnetic moments close to the spin-only value of 5.9  $\mu_B$ . These complexes are usually pale in colour as a result of the <sup>6</sup>A<sub>1g</sub> ground state and the occurrence of mainly spin-forbidden bands in the visible region of the spectrum. Thus, UV/Vis cannot provide reliable information about the fate of Fe(III) in zeolite matrices.

Unlike Al-, B-, or Ga-modified mesoporous silicas, where the nature and the coordination environment of the heteroatom can be probed with solid-state NMR spectroscopy [315-319], information about Fe-modified materials is scarce [196, 320]. From EPR studies of  $Fe^{3+}$  impurities in NH<sub>4</sub>-faujasite, Derouane et al [321] showed that iron can be simultaneously present in three forms:  $Fe^{3+}$  species in the aluminosilicate framework,  $Fe^{3+}$  ions acting as counterions and  $Fe_3O_4$  or another  $Fe^{3+}$  compound with strong exchange spin-spin interactions, precipitated on the zeolite. The synthesis, structure and characterization of a ferrisilicate analogue of a ZSM-5 zeolite was first reported in the open literature in 1985 [322]. By analogy with ferrisilicate analogues of zeolites described above, the Fe(III) in mesoprous MCM-41 can exist either as framework (FW) or extraframework species [323], and thus the structural arrangeme-
nt of the iron species is easily detectable by ESR techniques [324, 325]. Indeed, EPR spectroscopy has been successfully used to characterize the Fe species in Fe-MCM-48 [326,], Fe-MCM-41 [301, 308, 311], Fe-HMS [327] and Fe-Kenyaite [328]. In all cases, the ESR spectra of the as-synthesized (surfactant-containing) Fe-mesopore were dominated by two signals at g = 4.3 and 2.0, although additional peaks could be observed in certain instances. The assignment of these signals was based on previous literature on Fe-containing zeolites [321, 324, 329], according to which the signal at g = 4.3 corresponds to Fe(III) in a distorted tetrahedral environment whereas, that at g = 2.0 is attributed to Fe(III) in a highly symmetrical octahedral environment.

The ionic radii of  $Si^{4+}$ ,  $Al^{3+}$  and  $Fe^{3+}$  are 0.039, 0.057 and 0.067 nm, respectively [330]. From this difference in ionic size, it may be possible to deduce framework substitution in zeolites by XRD, where incorporation of the larger ion is expected to cause some amount of lattice expansion.

Other supplementary information on the location of Fe in MCM-41 can be obtained from temperature programmed reduction (TPR) studies. TPR has already been used to compare the redox properties of Fe incorporated in Fe-MCM-41 [331]. The materials were prepared by direct hydrothermal treatment of an Al-free recipe at 370 K for 170 h, and contained different framework iron contents. In samples with Si/Fe ratios of 20 and 12 all of the iron was found to be reducible with H<sub>2</sub>, but in materials with lower iron content only a part of the Fe(III) species could be reduced to Fe(II). In neither of the materials could Fe(III) be fully converted with CO to the divalent oxidation state. A significant part of the iron could be reversibly reduced and reoxidized in successive redox cycles. The TPR profiles of the prepared Fe-MCM-41 samples, pretreated in situ in a flow of  $O_2$ /He prior to the TPR runs, exhibited pronounced H<sub>2</sub> consumption in the same temperature range, between 520 K and 840 K.

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In the case of Fe-MCM-41(Si/Fe = 77) and Fe-MCM-41(Si/Fe = 139), *i.e.*, at low iron content, the areas of this TPR peak were found to correspond to reduction of only 76 and 66 % of the incorporated iron from the tri- to the divalent oxidation state, respectively. In contrast, the amount of consumed hydrogen calculated from the peak area in the TPR curve of Fe-MCM-41(20) corresponded exactly to that needed for the reduction of the incorporated iron to the divalent oxidation state. Reduction to zerovalent iron started at temperatures higher than 920 K. This points to the stabilization of the divalent iron species in MCM-41, since hematite was found to be completely reduced to metallic iron already at 920 K. The TPR curve of Fe-MCM-41(Si/Fe = 12) exhibited a second peak, starting at about 840 K, which was tentatively attributed to the reduction of extra-framework iron (EF-Fe) species. Furthermore, the H<sub>2</sub> consumption calculated from the main peak (between 500 and 840 K) slightly exceeded the value expected for the Fe<sup>3+</sup>  $\rightarrow$  Fe<sup>2+</sup> conversion. Possibly, part of the EF-Fe present in the form of large clusters, i.e., as iron oxide phases, may be reduced to the zerovalent state (see Table 1.2).

Table 1.2. Iron contents and H<sub>2</sub> consumption of different Fe-MCM-41 samples

Sample	Fe(mmol/g <sup>a</sup> )	$H_2$ consumption <sup>b</sup>	H/Fe (atom ratio)
		(mmol/g <sup>a</sup> )	
Fe-MCM-41(139)	0.119	0.039	0.66
Fe-MCM-41(77)	0.215	0.0817	0.76
Fe-MCM-41(20)	0.788	0.394	1.00
Fe-MCM-41(12)	1.254	0.677	1.08

<sup>a</sup>samples fired at 1273 K; <sup>b</sup>calculated from TPR peak between 500 and 840 K (ref. 331)

In any case, as from the TPR data, most of the iron incorporated into the pore walls of MCM-41 during hydrothermal synthesis is reducible to Fe(II) below 840 K. Only in low-iron-containing materials is a significant part of the iron resistant to reduction.

Mesoporous MCM-41 materials isomorphously substituted with iron were reported to be catalytically active in the conversion of N<sub>2</sub>O to NO [332], acetone to mesityl oxide and trimethyl-benzene [333], and SO<sub>2</sub> to SO<sub>3</sub> [334]. Other Fe-MCM-41-catalyzed oxidation reactions included the liquid-phase oxidation of cyclohexane with aqueous 30 % H<sub>2</sub>O<sub>2</sub> [335], hydroxylation of phenol using 30 % H<sub>2</sub>O<sub>2</sub> [336, 337], the epoxidation of styrene with H<sub>2</sub>O<sub>2</sub> [309, 338], and gas-phase CO oxidation [331]. Nonoxidative catalytic reactions include Friedel-Crafts benzylation of benzene with benzyl chloride [339], selective catalytic reduction (SCR) of NO with NH<sub>3</sub> [340], and ethylbenzene dehydrogenation [341].

Highly dispersed Fe<sub>2</sub>O<sub>3</sub> was incorporated almost exclusively into the mesoporous host (MCM-48) when prepared by impregnation [306], and showed a high catalytic activity in the methanol decomposition reaction, with high methane selectivity [342]. Direct hydrothermal synthesis of Fe-MCM-48 using a mixture of sodium laurate and CTAB as template, afforded an active catalyst for the hydroxylation of phenol [326]. The phenol conversion in this reaction was 43.6 % and the diphenol selectivity was 97.7 %.

# 1.4.2.2. Cobalt-containing Mesoporous MCM-41 (Co-MCM-41)

Because of its neutral framework, pure silica MCM-41 has had limited applications in catalysis, molecular sieving, catalyst supports, adsorbents, etc., [343]. However, an active catalyst can be prepared when the silicate framework of MCM-41 is modified by partial substitution with elements (or their oxides) such as Al, Ga, Fe, Ti, Pd, Mn, and Co [344-348]. Furthermore, high-metal-loaded CoMo/MCM-41 has been prepared by co-impregnation of MCM-41 with the metal precursors [349]. Jentys et al [348] have synthesized highly dispersed Co/MCM-41 catalysts by direct hydrothermal synthesis involving the addition of Co(II) ions directly to the synthesis gel. The degree of dispersion was confirmed by the XRD patterns of the resulting calcined

materials, which showed the absence of higher order metal oxide peaks (see Figure 1. 12):



Fig. 1.12. XRD patterns of Co/MCM-41 and MCM-41 [ref 348]

Interestingly, the small clusters of cobalt did not sinter during reduction or sulphidation. Incorporation of Co into the MCM-41 lattice was not observed. The addition of Co to the synthesis gel did not alter the structural characteristics of the MCM-41 samples. Co/MCM-41 was also prepared by solid-state ion exchange for comparison purposes. In addition, these authors have compared the structural properties of Co/MCM-41 prepared by direct synthesis and impregnation methods [350]. For both preparation methods the size of the metal particles decreased with the pore diameter (pore diameters between 2.9 and 3.6). Comparison of the Co/MCM-41 materials with the same pore diameter revealed that the direct synthesis method led to significantly smaller metal clusters than the impregnation method. MCM-41 materials functionalized by cobalt complexes have also been reported [251, 351]. The cobalt loading achieved in these studies, in which deposition is based on ion exchange, direct synthesis, or impregnation methods, was relatively low. To increase the Co loading,  $Co_2(CO)_8$  was deposited onto Si-MCM-41 surface [352] from the gas phase in a fluidized bed reactor, and loadings of up to 41 wt% Co were achieved using a pulse deposition method. A multi-stage grafting method has been used to immobilize optically-active Co(II) salen complexes in MCM-41 [353]. These materials showed a very high enatioselectivity in the asymmetric borohydride reduction of aromatic ketones, as compared to similar homogeneous salen catalysts.

Highly dispersed Co-Ru nanoparticles in mesoporous silica xerogels and MCM-41 were also prepared by impregnation from organic solutions of heterometallic carbonyl clusters [NEt<sub>4</sub>][Co<sub>3</sub>Ru(CO)<sub>12</sub>] [354], followed by thermal treatment under an inert atmosphere. Co/MCM-41 [355] and Ru-promoted Co/MCM-41 [356, 357] have been prepared by Goodwin Jr's group, and showed activity towards CO hydrogenation reactions (i.e. the Fischer-Tropsch reaction). 5 % Co/SCMM (SCMM = silicate crystalline mesoporous material) prepared by impregnation with  $Co_2(CO)_8$ from its hexane solution under a deoxygenated atmosphere, also showed high CO conversion in FTS compared to that based on silica gel [358]. On the other hand, high-metal-loaded CoMo/MCM-41 materials prepared by coimpregnation have proved to be substantially more active than conventional CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts [349] in the hydrodesulphurization (HDS) of dibenzothiophene in distillate fuels. A monometallic cobalt-containing mesoporous smectite-like material [SM(Co)] prepared by a hydrothermal method was active as a catalyst for the hydrodesulfurizat-ion (HDS) of thiophene [359], and the addition of platinum to this system was found to enhance the HDS activity by 50 % with no significant change in the product distribution. Thus, the synthetic Co-containing smectite-like material is an active catalyst for the thiophene HDS reaction. Cobalt was also loaded onto SiO<sub>2</sub> by wet impregnation using a cobalt acetate solution and comparative studies showed that the activity of SM(Co) was much higher than that of Co/SiO<sub>2</sub>.

Ramírez et al [360] prepared CoMo HDS catalysts supported on alumina with different amounts of aluminium-modified MCM-41 by pore volume impregnation from aqueous solutions of Co and Mo precursors. The materials were tested in the dibenzothiophene (DBT) hydrodesulfurization reaction. The results showed that the incorporation of MCM-41 into the catalyst formulation leads to higher catalytic activity. The TPR results indicated a diminished interaction of the Co and Mo phases with the support, compared to those existing in the alumina-supported catalyst. The decrease in surface area indicates that under the conditions of impregnation, the Mo and Co metal salts are not adequately dispersed. This lack of dispersion, which under calcination causes the partial blockage of the MCM-41 pores, may be due to the isoelectric point of the MCM-41 (pH = 2.3) being below the pH of the impregnating solution (pH = 5.5) (see Figure 1.13)



Figure 1.13. Zeta potential of MCM-41 as a function of pH. The dotted line indicates the isoelectric point (ref. 360).

Under this preparation condition, the surface of the MCM-41 is negatively charged, and therefore, the molybdate anions do not readily adsorb on the surface causing

some agglomeration of the Mo phases. This result is in line with the behaviour of pure silica supports, on which the molybdenum ions cannot be well dispersed. In order to envision the type and reducibility of the Co and Mo species present in the catalyst precursors, TPR experiments were performed and the corresponding reductograms observed are shown in the Figure 1.14 below:



Figure 1.14. TPR patterns of CoMo/Al-MCM(x) catalysts, x is the weight % of MCM-41 in the support [ref. 360].

For a pure alumina-supported catalyst, two main reduction peaks are observed and are assigned to the reduction of octahedral Mo species (peak at  $T_{max} = 706$  K), and tetrahedral Mo species in strong interaction with the alumina support (peak at  $T_{max} = 1040$  K). Also observed is the presence of shoulders at 773 K, due to the reduction of polymeric octahedral Mo species, and at 1004 K, due to the second reduction step of

octahedral Mo species. The reduction of Co species takes place at about 873 K. As MCM-41 is incorporated into the support, a decrease in the peak assigned to the reduction of tetrahedral Mo species in strong interaction with the support is observed. The maximum of this reduction peak is, therefore, shifted towards 973 K, where the reduction associated with the second reduction step of octahedral Mo(VI) takes place. In line with this, a significant increase in the size of the two low-temperature peaks corresponding to octahedral Mo species is observed. In fact, the magnitude of the reduction peak at about 773 K increases so much that a change in the relative size of the two low-temperature peaks is clearly evident. In line with the above, the total hydrogen consumption, and therefore, the reducibility of the Co and Mo species, increases with MCM-41 loading. These results indicate a clear shift in the population of Mo species, from tetrahedral to octahedral ones, as the MCM-41 content is increased in the catalyst support. The TPR traces also show an increase in the hydrogen consumption in the region around 873 K, where the Co species are reduced. This indicates that the population of reducible Co (Co in octahedral coordination) also increases with MCM-41 content. This observation is well in line with the results obtained with Co/SiO<sub>2</sub> catalysts, in which the Co species remain in octahedral coordination and are easily reducible. In contrast, in alumina-supported catalysts part of the Co forms tetrahedrally coordinated CoAl<sub>2</sub>O<sub>4</sub>, that is hard to reduce. Clearly, the higher total hydrogen consumption, due to increased reduction of both Co and Mo, observed in MCM-41-containing catalysts, is due to a shift in the type of Co and Mo species from tetrahedral to octahedral ones. This result is clearly related to the milder interaction of the metal phases with the MCM-41 in the support compared to the alumina-supported catalysts. This milder interaction of the Mo and Co species with the support may induce interactions between Mo and Co. Because of this, the formation of species such as CoMoO<sub>4</sub> cannot be discounted, especially when the form and position of the maximum of the TPR peak observed at 771-785 K and the shoulder at about 973 K are noted. These features coincide with the data reported by Arnoldy et al [361] for the reduction of CoMoO<sub>4</sub>, which reduced in two steps, leading to two reduction peaks at 790 and 980 K. The observed increase in hydrogen consumption

with MCM-41 content would also be in line with the presence of an increased amount of reducible Co, in the form of CoMoO<sub>4</sub> or other reducible Co species, at the expense of Co in CoAl<sub>2</sub>O<sub>4</sub>, which is hardly reducible.

## **1.4.3.** General Catalytic Reactions of Mesoporous Materials

It has already been mentioned that Si-MCM-41 materials possess a neutral framework, which limits their practical utility [343]. Since most of the applications of silicate type of materials are in the field of catalysis, the catalytic properties can be adjusted by the incorporation of different metals such as titanium and aluminium into the MCM-41 framework [63, 362, 363]. The acidity of aluminosilicate MCM-41 materials is of medium strength when compared to USY zeolite [363].

Some of the reactions catalyzed by metal-containing MCM-41 materials are: selective oxidation of hydrocarbons using Ti-MCM-41 [362], catalytic oxidation of aromatic compounds using Ti-MCM-41 [63], liquid-phase oxidation of hydrocarbons using Zr-MCM-41 [364], n-hexane aromatization using Ga-MCM-41 [365], peroxidative halogenation using Ti(IV)-grafted MCM-41 and MCM-48 [366], hydrocracking of vacuum gasoil using NiMo/MCM-41 [367], hydrogenation of aromatics in diesel fuels on Pt/MCM-41 [284], alkylation of naphthalene with alcohols over mesoporous MCM-41 [368], epoxidation of cyclohexene and pinene with tetrabutylperoxyhydroxide (TBHP) on Cp<sub>2</sub>TiCl<sub>2</sub>-grafted MCM-41 [298], Knoevenagel condensation with aminopropyl-functionalized MCM-41 [228], selective synthesis of jasminaldehyde at low benzaldehyde to heptanal ratios using aluminosilicate MCM-41 [369], Knoevenagel and Michael condensations using alkali-MCM-41 [347], etc.

### **1.5. Pollution Control Through Catalysis**

One of the most significant problems facing mankind relates to the quality of our environment. All environment-related issues are multidisciplinary, ranging from science and engineering to social, economic and regulatory issues [371]. Furthermore, these issues are global in nature, requiring multidisciplinary, multiorganizational and multinational educational efforts. Pollution is one such problem directly affecting the environment and the quality of life. The effects of pollution, leading to health and other problems in certain parts of the USA (notably in California), were recognized as long ago as the 1950s. The recognition of photochemical smog as a major contributor to these problems, and the part played by the motor vehicle, led to the formulation of the US Clean Air Act of 1970. This act laid down a programme to reduce emissions from motor vehicles by 90 % compared with an average 1960 model car. Initially, some improvements were achieved by engine modifications, but this did not achieve the target levels and alternative technologies needed to be considered. Catalysts had already been evaluated as possible solutions to the problem, but had been rejected because of their short lifetime. Both base metal and precious metal catalysts were very susceptible to the presence of lead additives in the fuel, and the sulphur oxides generated when the fuel-bound sulphur was combusted in the engine. It was eventually agreed that catalysts could be successful, provided fuel without lead additives was used. This required the setting up of a distribution chain for the socalled 'unleaded' fuel, and finding alternative solutions to problems of valve wear caused by the removal of the lead additive.

In short, many of our current pollution problems are associated with the energy technologies that rely on the combustion of carbon-based fuels [371]. These involve the emission of greenhouse gases, acid rain precursors (NO<sub>x</sub> and SO<sub>x</sub>) and carbon monoxide, formation of photochemical oxidants and mining-related pollution. Thus, it is a general society aim to make environmental issues a major factor in process

design considerations, particularly in the design of highly active pollutant-abatement catalysts and to minimize the level of these toxic emissions.

# 1.5.1. Carbon Monoxide Poisoning

Carbon monoxide is an invisible, odourless, colourless, tasteless and poisonous gas that is widely known as the "silent killer" because it cannot be detected by human senses. When inhaled, CO is rapidly absorbed by the lungs into the bloodstream where it diffuses rapidly across the alveolar capillary membrane and binds tightly to iron centres in hemoglobin and other hemoproteins. CO induces its toxicity effects by binding to hemoglobin with an affinity 240 times greater than oxygen, to form carboxyhemoglobin [372, 373], i.e. the oxygen-carrying oxyhemoglobin (O<sub>2</sub>Hb) is replaced by the more stable carboxyhemoglobin (COHb), which decreases the blood oxygen content and hinders the allosteric release of oxygen from hemoglobin to tissues. Carbon monoxide can be lethal at concentrations of less than 0.1 % and the kinetics and mechanism of its toxicology has been described elegantly by Coburn et al [374].

Sources of carbon monoxide include incomplete combustion of burning fuels like natural gas, liquid propane gas, gasoline, kerosene, oil, coal, wood, charcoal and even tobacco. Automobiles, with their internal combustion engines, are the primary sources of CO pollution and the most dangerous when parked inside a garage. Carbon monoxide emissions from modern engines, though controlled by regulatory standards, are still highly toxic in poorly ventilated spaces [375]. CO oxidation is an efficient way to remove traces of CO from the exhaust emissions at low temperatures, and will be discussed in the sections that follow.

## 1.5.2. CO Oxidation and Catalysis by Gold

Typical emissions in the exhaust of gasoline-powered engines consist of noxious gases such as carbon monoxide (CO), unburned hydrocarbons (HC) and oxides of nitrogen (NO<sub>x</sub>). These are effectively controlled by adoption of a three-way catalytic converter (TWC) whereby the three gas types are oxidized or reduced to harmless carbon dioxide (CO<sub>2</sub>), nitrogen (N<sub>2</sub>) and water vapour (H<sub>2</sub>O). The name three-way catalytic converter derives from the fact that three different components of the automobile emissions are controlled simultaneously by a catalyst [376]. Pt and/or Pd and Rh are the most common active phases in three-way catalysts. The role of platinum in the TWC is to oxidize the CO and hydrocarbons (HC), especially during cold start-up of the engine. Rhodium is active to reduce nitrogen oxides (NO<sub>x</sub>) especially in the presence of a high concentration of CO [377].

However, the catalytic converter cannot effectively remove HC and CO from the outlet of internal combustion engines in the cold-start phase of running the engine, and these emissions must be reduced to meet new regulations and improve the environment [378]. The cold-start period refers to the first few minutes after engine ignition before the catalyst reaches its light-off temperature (250-300 °C), during which 50-80 % of the total unburned hydrocarbon fuel simply passes out of the tailpipe into the atmosphere. The light-off temperature is defined as the temperature at which a catalyst becomes functional.

Over the years, significant effort has been put in improving the cold-start behaviour [379] of catalytic converters around the world. Examples of new technologies that have been developed include close-coupled catalysts [380], electrically-heated catalysts (EHC) [381-383] and hydrocarbon traps [384-386]. The major advantage of close-coupled catalysts is that no additional power is needed. However, the volume of catalyst connected to the engine must be less than 200 ml and must be "warmed-up" rapidly. A large quantity of noble metal must also be used to achieve high

purification. The cost of a catalyst is directly linked to that of noble metals, which are generally very expensive. The EHC technique has attracted wide attention since catalysts can be rapidly heated and the light-off time is shorter than 40 s. The major disadvantage of the EHC technique is that the EHC carrier material is made of metals which have low electrical resistivity (~10<sup>-5</sup>  $\Omega$ .cm) and high thermal conductivity, so high power (> 1.5 kW) and therefore, high current (>150 A) are usually required [387] for EHC to take effect and achieve reasonable cold-start behaviour. Such high current and power are not available from present vehicle power systems, and consequently the EHCs have not been deployed because these devices are cost- and energy-intensive. The HC trap technique involves a complex preparation of a hydrocarbon absorber, which makes them impractical in the near future.

It is thus of interest to develop a highly active CO oxidation catalysts to remove trace amounts of CO at low temperatures according to the following reaction:

$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$
,  $\Delta G_{298} = -257.1 \text{ kJ/mol}$ 

Gold has long been regarded as catalytically far less active than platinum group metals [388-390], and has consequently found very little application in heterogeneous catalysis. This inactivity or unreactivity has its origins in its electronic structure, ([Xe] 4f<sup>14</sup>5d<sup>10</sup>6s<sup>1</sup>), since gold has a filled d-band, and filled bands are usually associated with low activities [391]. The other factor normally cited as a cause for the unreactivity of gold is its high electronegativity, which makes it unable to form stable compounds with other electronegative elements such as oxygen and sulphur [392]. However, the realization by Haruta and coworkers [393, 394] that the nobleness of gold breaks down at nanometric sizes when it is in contact with reducible oxidic supports, has triggered global interest in the use of gold as a catalyst. In this pioneering work, Haruta and coworkers [393, 394] showed that gold is remarkably active for low-temperature CO oxidation when it is highly dispersed and deposited on supports

such as reducible semiconductor metal oxides, hydroxides of alkaline earth metals, or amorphous ZrO<sub>2</sub>.

Since the initial results on CO oxidation suggested the importance of the nature of the support on the resulting catalytic activity, two different classes of supports have been identified: (i) active supports are materials that are relatively easy to reduce like  $Fe_2O_3$  or TiO<sub>2</sub>, and (ii) inert or inactive supports like Mg(OH)<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>. Although active supports often result in very active gold catalysts, inert supports can, in some cases, lead to catalysts as active as those with reducible supports, but it is very important to ensure a high dispersion of very small particles of gold on the oxide [395, 396]. In general, silica supported gold samples were found to be less active than the alumina-supported ones [397], probably due to the presence of large gold particles.

Since this breakthrough discovery, much attention has recently focused on the use of gold as a catalyst [398, 391], and below are some of the heterogeneous reactions that are catalyzed by gold [399]:

- •Hydrochlorination of ethyne
- •Oxidation of CO and hydrocarbons
- •Selective oxidation, eg epoxidation of olefins
- •Selective hydrogenation
- •Hydrogenation of CO and CO<sub>2</sub>
- •Water gas shift
- •Reduction of NO with propene, CO or H<sub>2</sub>
- •Reactions with halogenated compounds
- •Hydrogen plus oxygen reaction
- •Removal of CO from hydrogen streams

## **1.5.3.** Commercial Applications of Gold Catalysts

Gold catalysts have already been commercialized to remove domestic odour and CO in air at room temperature [400]. Catalysts for the oxidation of carbon monoxide at low temperature also find practical applications in several devices: active catalysts are used in closed-cycle CO<sub>2</sub> lasers, in gas sensors for detection of trace amounts of CO in air, in CO safety masks, etc., [401-403]. Gold-palladium alloy catalysts are used in the commercial production of vinyl acetate monomer (VAM) by BP Chemicals at Hull (UK) using a new 'Leap Process'. This monomer is used in the manufacture of emulsion-based paints, wallpaper paste and wood glue [404]. Possibilities are being investigated for putting some gold in car engines or to have twin catalysts, gold and platinum with the former covering the cold period and platinum the hotter one [405]. A future is also envisaged for using gold in fuel cell systems [406], and this application is on the verge of a breakthrough in Europe [406].

# 1.5.4. Supported Au Catalysts

The high reactivity of gold nanoparticles has been a subject of many studies since its discovery by the group of Haruta in the eighties [393, 394]. Several studies have pointed out different factors as responsible for the enhancement of the reactivity observed mainly in oxidation processes. However, some questions related to the role of the support, the existence of charged atoms at the interface and the availability of low coordinated sites have yet to be answered.

Gold can be highly dispersed on a variety of metal oxides by coprecipitation and deposition-precipitation [394] preparative techniques, followed by calcination in air. Such supported gold differs in catalytic nature from unsupported gold particles and has been found to exhibit high catalytic activities for low-temperature oxidation of CO. The TEM photograph of the highly dispersed Au/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> prepared by coprecipitation is shown in Figure 1.15 below:



Figure 1.15. TEM micrograph of Au-Fe(1:19) coprecipitate calcined at 400 °C: dispersion of gold particles over  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> [ref. 394].

Figure 1.16 (*see below*) compares the catalytic activities for the oxidation of H<sub>2</sub> and CO of unsupported gold particles with diameters around 20 nm, and gold supported on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> alone. The corresponding Arrhenius plots and the calculated activation energies of the representative gold catalysts on different supports, for the CO oxidation results in Figure 1.16, are shown in Figure 1.17.



Figure 1.16. Conversions of H<sub>2</sub> and CO in catalytic oxidation reactions as a function of catalyst temperature. CO or H<sub>2</sub> 1 vol% in air, SV =  $2 \times 10^4$  h<sup>-1</sup>.ml/g-cat: oxidation of H<sub>2</sub>( $\circ$ ) and CO( $\bullet$ ) on Au-Fe(1:19) coprecipitate calcined at 400 °C in air; oxidation of H<sub>2</sub>( $\Box$ ) and CO( $\bullet$ ) on Au powder prepared from colloidal metal particles with diameters around 20 nm; oxidation of H<sub>2</sub>( $\Delta$ ) and CO( $\bullet$ ) on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> powder prepared by calcination of ferric hydroxide at 400 °C. [ref. 394]



Figure 1.17. Arrhenius plots for the rate of CO oxidation over supported catalysts: ( $\blacktriangle$ ) Au(1.2 wt%)/Co<sub>3</sub>O<sub>4</sub>, ( $\Box$ ) Au(0.66 wt%)/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, and ( $\circ$ ) Au(3.3 wt%)/TiO<sub>2</sub>. [ref. 394]

It can be seen from the Arrhenius plots above that the activity of Au catalysts is influenced by the type of oxidic support used, with the cobalt-based catalyst exhibiting the lowest activation energy for the oxidation of CO.

# 1.5.5. Preparation of Supported Au Catalysts

The use of gold as a catalyst requires a careful and unconventional preparation of the gold metal, centred on achieving a very small gold particle size. Preparation methods like co-precipitation (CP) [393, 407, 408], deposition-precipitation (DP) [394, 409], chemical vapour deposition (CVD) [396, 410], adsorption of gold colloids [411], supporting gold phosphine complexes on as-precipitated metal hydroxides [412] and co-sputtering [413] can produce highly dispersed gold catalysts, which exhibit unique catalytic nature in many different reactions depending on the type of metal oxide supports used [414, 415]. The latter methods are more demanding and less suitable in the production of larger quantities of materials, and therefore uneconomic. Indeed the most popular and reliable synthesis methods to prepare supported gold catalysts are the initial methods reported by Haruta and coworkers [393, 414], namely coprecipitation and deposition-precipitation, which result in highly dispersed and highly active supported gold catalysts for low-temperature oxidation of CO. In the light of the coprecipitation method, Wagner et al [416] coined the name "inverse coprecipitation" for the preparation method involving a reversed order of addition of the coprecipitate precursor solutions.

Haruta [414] has shown that a strong interaction between the support and the Au particles is necessary to avoid the coalescence of particles to form bigger and inactive crystallites. This is normally achieved by using the coprecipitation method, although this method has the drawback of leaving part of the gold particles buried inside the support and inaccessible to the reactant gas stream. Therefore, a preparation method is still needed to produce almost all gold particles being accessible to the reactants.

Typically, coprecipitation or deposition-precipitation methods are more desirable than impregnation, especially when chloroauric acid (HAuCl<sub>4</sub>.xH<sub>2</sub>O) is used as the precursor. Various processing variables in the synthesis of supported gold catalysts have been studied, which include pH, temperature and concentration of the preparation solution, calcination temperature, reduction temperature, and reduction/oxidation cycling. Some of these studies have helped elucidate the underlying chemistry that causes variation in the properties of the final solid.

One of the better understood variables in the deposition-precipitation procedure is pH. In such a preparation method, HAuCl<sub>4</sub> is used as the metal precursor. The chloroauric anion hydrolyzes in solution to produce  $Au(OH)_xCl_{4-x}$ . The extent of hydrolysis depends on the pH, as well as Au and Cl concentrations [417]. It has been found that, depending on the oxide support, catalyst preparation at a pH ranging from 7 to 8 is preferable [418]. At this pH, the value of x is close to 3. At lower pH values, when there is less hydrolysis of the Au-Cl bond, large Au particles are formed after calcination [414]. At pH values above the isoelectric point of the oxide, adsorption of the negatively charged  $Au(OH)_xCl_{4-x}$  complex decreases rapidly. Therefore, there is a narrow range of pH values where sufficient Au can be deposited onto the support with minimal chloride in the Au complex. It is interesting to note that in order to obtain a high dispersion of Au in the final catalyst, it is desirable that the precursor Au complex is adsorbed as an anion. If the  $AuCl(OH)_3^-$  precursor is added to a dilute suspension of the support while keeping the pH at 7, Au(OH)<sub>3</sub> would be the predominant species due to the low initial chloride concentration [417]. Its low solubility causes precipitation onto the support material, resulting in a poor catalyst.

Recently, another effect of the pH of the solution was identified [419]. In addition to  $Au(OH)_xCl_{4-x}$ , Cl<sup>-</sup> ions are also adsorbed onto the oxide support. The amount of chloride adsorbed decreases rapidly as the isoelectric point is approached (alumina support), when the oxide surface is no longer positively charged. The adsorbed Cl<sup>-</sup> has two effects: (1) it causes agglomeration of Au particles during calcination, such

that the average Au particle size is larger in samples with a higher residual chloride content, and (2) it inhibits the catalytic activity by poisoning the active site. The adsorbed chloride can be displaced by other anions. In the earlier preparations, magnesium citrate was added to the preparation solution to obtain an active catalyst [420]. It is believed that the primary function of the citrate is to displace the chloride from the support and possibly from the Au(OH)<sub>x</sub>Cl<sub>4-x</sub> complex. Chloride can also be removed by reduction or calcination [421, 422]. However, high temperature calcination or reduction causes agglomeration of Au particles.

More recently, attention has turned to the effect of calcination temperature as a factor influencing the activity of supported gold catalysts. Haruta et al [393, 394, 423] found that coprecipitated gold on iron oxide is active only after calcination at 400 °C. At this temperature the gold forms small metallic particles that are the active species. However, Tanielyan and Augustine [424] prepared coprecipitated Au on iron oxide catalysts that were already active after drying at 95 °C, whereas calcination at high temperature (380 °C) led to a significant decrease in activity. These contradictory observations suggest that the role of calcination in the preparation of the catalysts is still unknown. On the other hand, Kozlova et al [425] studied a series of samples prepared by impregnation of several iron oxide supports prepared from the same precursors but with different water or hydroxyl group content. The activity of these catalytic systems, even after calcination, has been found to decrease as the amounts of water and hydroxyl groups decrease before impregnation with the gold precursor. It was reported that for Au/TiO<sub>2</sub> [426, 427], Au/iron oxide [427-429], and Au/MnO<sub>x</sub> [430] catalysts, calcination at a mild temperature (100-200 °C) resulted in more active catalysts than calcination at higher temperatures. There are also reports that uncalcined Au/Al<sub>2</sub>O<sub>3</sub> [418] or Au/Y [431] can be very active.

The activity of Au/TiO<sub>2</sub> and Au/ZrO<sub>2</sub> CO oxidation catalysts prepared by adsorption of gold colloids on a support was also found to be influenced by the calcination temperature [432]. Maximal activity was obtained for the catalysts calcined at 500  $^{\circ}$ C

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(Au/TiO<sub>2</sub>) and 560 °C (Au/ZrO<sub>2</sub>), respectively. Catalysts calcined at higher temperatures exhibited lower activity due to sintering of the gold particles (T > 600 °C), as metals on supports are theoretically mobile at their Tammann temperature (for gold,  $T_{Tammann} = 395$  °C). As a consequence of the low melting point and high surface mobility of gold, interest has focused on preparation methods which minimize gold agglomeration [412]. To prepare gold of high dispersion, Guillemot et al, Kang et al, and Ichikawa et al have used the zeolites Y [433-439] or MFI (ZSM-5) [440, 441]. The catalysts were probed for the decomposition and reduction of nitric oxide and the oxidation of carbon monoxide.

For the preparation of highly dispersed gold catalysts on zeolitic supports, different synthetic methods have also been used, which also differ from the unconventional synthetic methods mentioned above. These include: cation exchange of the iron-impregnated zeolite-Y with chloroauric acid solution [442], autoreduction of Au<sup>3+</sup> by ethylenediamine ligands inside NaHY [433], co-exchanging iron(II)ethylenediammonium and Au(III)ethylenediamine complex ions in HY [443] and sublimation of AuCl<sub>3</sub> onto MFI [444].

In spite of the success with some inert supports, the preparation of active Au/SiO<sub>2</sub> catalysts with solution-based methods is difficult, and the resulting materials have very low activity in CO oxidation [396, 418]. In the case of SiO<sub>2</sub>, the CP and DP techniques fail to poduce active CO oxidation catalysts, because the point of zero charge (PZC) of SiO<sub>2</sub> is around pH 2, and at pH 7 this oxide exhibits a large negative surface charge, which prohibits the deposition of Au(OH)<sub>3</sub>. Impregnation of SiO<sub>2</sub> with HAuCl<sub>4</sub> [396] or cationic Au-phosphine cluster solutions [445] produced very large supported Au particles (mean size  $\geq$  16 nm), which were inactive for CO oxidation at room temperature even after calcination. However, the use of amines as stabilizers of the gold metal phase during the sol-gel deposition of Au on SiO<sub>2</sub> resulted in the formation of catalytically active Au particles with an average size of 5-6 nm [446, 447]. Chemical vapour deposition (CVD) was also successfully applied to

prepare small (mean size *ca*. 6.6 nm) and active silica-supported gold particles, which showed CO oxidation activity even at subambient temperatures [396]. Also, functionnalizing the mesoporous SiO<sub>2</sub> surface with cationic organosilanes to generate a monolayer of positively charged groups on the pore surface [448], as well as stabilizing the Au particles by using self-assembled monolayers (SAMs) to surround the particles [449, 450] give small active silica-supported gold nanoparticles. This provides evidence that SiO<sub>2</sub> can also be a useful support for catalytically active gold nanoparticles. Recently, the attractiveness of silica materials as supports for gold catalysts has increased following reports on Au particle growth within the channels of MCM-type mesoporous silicas [451].

# 1.5.6. Controversy over the active species in CO oxidation

The outstanding activity of highly dispersed gold in the low temperature CO oxidation on supports like  $TiO_2$ ,  $Fe_2O_3$ ,  $MnO_x$ ,  $ZrO_2$ , etc. has been the subject of several review articles [391, 412, 414, 415, 452].

Although active catalysts commonly contain small, 2-5 nm Au crystallites, size alone does not seem to be a sufficient factor for the high activity of supported Au catalysts in CO oxidation [418]. The actual cause of this high activity is still uncertain, and there is a wide variation in the activities reported among different laboratories for apparently similar catalysts. There have been a number of proposals as to the active catalytic site, which include: gold-support interface [394], small Au clusters that possess nonmetallic electronic properties due to quantum-size effects [453], and surface step and strain defects [454]. A chemical model that involves an ensemble of metallic Au atoms and Au cations with hydroxyl ligands has been suggested [455-457]. There appears to be increasing support that the active site involves the perimeter of the Au particles or the Au-support interface [426,458, 459]. Although there is still an ongoing debate on what causes the high activity of finely dispersed gold on oxide carriers [391, 411, 414, 453, 454, 460-462], it is well accepted that the

final activity of gold is dependent on the particle size, on the support properties (e.g. semiconducting or insulating), the preparation procedure, and the pretreatment [391, 411, 414, 460, 462]. On the other hand, Finch et al [463] have attributed the room temperature activity of the Au/Fe<sub>2</sub>O<sub>3</sub> catalysts to a synergistic interaction between AuOOH.xH<sub>2</sub>O and a ferrihydrite species.

To summarize, supported gold catalysts [464] are very active for CO oxidation and other environmentally important reactions when: (i) there is strong contact between the support and the gold particle perimeter, (ii) there is an appropriate metal oxide support, and (iii) the particle size is < ca. 5 nm. Three broad areas for the new applications of gold catalysts have been identified [465]: (a) Automotive pollution control (cold-start, diesel engines), (b) Clean energy generation (fuel cells, hydrogen purification, electrocatalyst extender, etc.) and (c) Environmental pollution control (odour abatement and toxin removal; air conditioning in automotive, aircraft, submarines, office buildings, hospitals, factories and restaurants; waste incinerators; gas masks).

The mesoporous gold-silica nanocomposite materials of the MCM-41 type are expected to be potentially useful as sensors and catalysts.

# 1.6. Hypotheses and Aims of the study

Nanoscience developments are increasingly being applied in catalysis to prepare materials and develop structure-performance relationships. Precisely controlling size, shape, spatial distribution, composition, and thermal and chemical stability of the active catalyst nanocomponents can provide catalysts with selectivity approaching 100% and very high activity plus low process energy consumption. The Mobil meso-porous material, MCM-41, possesses a myriad of catalytically sought-for properties, including high BET surface area, narrow pore size distribution, large pore sizes and high hydrocarbon sorption capacity. These properties make it a promising support for

active metal components in various fields of heterogeneous catalysis. Combining these properties of mesoporous MCM-41 with the unrivalled low temperature activity of gold can result in highly active, easily prepared nanocomposite catalysts.

It is thus the aim of this thesis to study the preparation parameters for Au-based mesoporous MCM-41-supported catalysts for the total oxidation of CO at low temperatures. Starting with MCM-41 in its pure silica form, as well as starting with metal precursors at the synthesis stage of MCM-41, we hope to prepare Fe- and Co-MCM-41 materials with maximum retention of the important properties of the mesoporous silicate. The presence of such base metals within the silicate framework is expected to induce reducibility, strengthen the material, etc. *The base metal-modified MCM-41 materials are to be used as supports for Au catalysts*, which are known to catalyze the oxidation of carbon monoxide at low temperatures. The principal role of the Fe or the Co component is to aid in the redox reactions of Au, and to provide anchoring sites for the gold nanoclusters in order to reduce their chances of coalescing during calcination above their Tammann temperature (395 °C). The use of this high surface area support should be beneficial in keeping the loading of precious metals, because of their high prices, low but yet achieve reasonable catalytic activity.

## 1.7. Rationale/Motivation for Research in this Thesis

Carbon monoxide (CO) and unburned hydrocarbons (HCs) are ubiquitous pollutants in the air, arising from incomplete combustion in gasoline-powered car engines. CO is of immediate environmental and public health concern as even small exposures (ppm levels) can be lethal. This gas effects its toxicity by binding to hemoglobin with an affinity of 240 times that of oxygen, and thus reduces the oxygen-carrying capacity of the red blood cells by forming a more stable carboxyhemoglobin (COHb). It is thus desirable to achieve 100% oxidation of these pollutants to  $CO_2$  and  $H_2O$ through catalytic oxidation. New stricter emission control regulations for exhaust gases and the high cost of the PGMs used in TWCs have led to investigations to

reduce the cost of these catalysts by improving their activity and durability. The present formulation of the TWCs, comprised of PGMs, is inefficient for these oxidation processes at ambient temperatures (during the engine's cold-start phase), and only become effective when their temperature is above 250 to 300 °C (known as the light-off temperature). Therefore, new catalyst designs are necessary to take care of these noxious emissions at low temperatures.

The realization that highly dispersed nanoparticulate Au on reducible oxide supports can accomplish the oxidation of CO oxidation at room temperature and in the presence of moisture (which is not the case with other metals), opens up a space for Au in automotive pollution control during the cold-start phase of running the engine. In South Africa, the project AuTEK has been launched as a joint research venture between AngloGold and Mintek, which focuses on the application of gold in catalysis for combating air pollution by removing noxious gases such as CO and NO<sub>x</sub>. Thus, a detailed study of the various preparation parameters for active Au catalysts in CO oxidation reactions is in line. However, due to the limitation with the price of Au precursors, it is desireable to use economic amounts of Au in the catalyst formulations (~1-3 wt% Au). This can be achieved by employing a porous support of reasonably high specific surface area. The Mobil mesoporous material, MCM-41, matches this requirement and will be explored as support for Au catalysts, which can be used to purify the air in office buildings, aircraft and for the general remediation of air pollution.

The relatively greater availability of gold compared to the PGMs and the skyrocketing prices of platinum and palladium since 1998 [465, 466], are also a good motivation for carrying out extensive research with Au-based systems in order to improve the price of this metal. In his paper entitled "The Golden Age of Catalysis", G. C. Bond [467] backs up this motivation and further revolutionizes gold-based research with the words, "We may confidently expect further developments, and early in the new millennium gold should take its place alongside its neighbours as a vital member of the armoury of transition metal catalysts".

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