High nickel- and titania-containing mesoporous silicas: synthesis and characterisation

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High Nickel- and Titania-containing Mesoporous Silicas:
Synthesis and Characterisation

by

Wei Wang

A doctoral thesis submitted in partial fulfilment of the requirements for the award of
Doctor of Philosophy of Loughborough University
2005

Supervisor: Dr. M. Song

Institute of Polymer Technology and Materials Engineering
Loughborough University

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Abstract

In order to heighten the nickel content in mesoporous silica frameworks, a new direct synthesis method, called modified DS method, has been developed instead of the commonly used direct synthesis method. In addition, with the aim of incorporating a high amount of titania into SBA-15 mesoporous silica without blocking its mesopores, a multistep impregnation method, called the MSI method, has also been developed. By using the two developed methods, high nickel- and high titania-containing mesoporous silicas obtained were synthesized. The nickel- and titania-containing mesoporous silicas were characterised by various techniques, i.e. XRD, TEM, EDX, SEM, \( \text{N}_2 \)-sorption, XPS, FTIR, UV-Vis-DRS, UV-VIS, TPR, and Raman spectroscopy.

For nickel-containing mesoporous silicas synthesized by the modified DS method, satisfactory mesostructures were obtained and the nickel content was increased up to 14.7 wt.%. So far, no reports have been published on synthesis of mesoporous MCM-41-type silica with higher nickel content than 3.6 wt.% using DS method. Via our modified DS method, high BET surface area (\( >840 \text{ m}^2/\text{g} \)) and pore volume (\( \geq 0.73 \text{ cm}^3/\text{g} \)) were also achieved. Nickel was found to be incorporated into the silica frameworks. Formation of nickel phyllosilicates was also confirmed. After activation, mesostructures were still intact. Small nickel clusters embedded in the silica walls were found.

A high amount of titania (up to 24.4 wt.%) was incorporated into the mesoporous SBA-15 silica via the multistep impregnation method. No damage to the SBA-15 silica mesostructures was caused. The existence of small titania nano-domains was confirmed to be present by Raman and UV-vis-DRS measurements. High dispersion of them was realized via this method according to the results of low-angle XRD, TEM and \( \text{N}_2 \)-sorption measurements. Importantly, no blockage of mesopores was observed. Photo-activity tests showed the superiority of the materials synthesized by the MSI method to those by one-step impregnation method.
Keywords: nickel; titania; mesoporous; microporous; silica; nanoclusters
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Abbreviation list

Chemicals:

- CTAB: cetyltrimethylammonium bromide
- CTAC: cetyltrimethylammonium chloride
- EDTA: ethylene diamine tetraacetic acid
- EG: ethylene glycol
- MTMO: mesoporous transition metal oxide
- TBOT: tetra butyltitanate
- TEOS: tetraethyl orthosilicate
- TMAOH: tetramethyl ammonium hydroxide
- TMB: mesitylene
- TMI: transition metal ions
- TRMS: trimethysilane
- TTIP: titanium tetra isopropoxide

Synthesis method:

- CVD: chemical vapour deposition
- DS: direct synthesis
- EISA: evaporation induced self-assembly
- MSI: multistep impregnation
- OSI: one-step impregnation

Characterisation techniques:

- EDX: energy dispersive X-ray spectroscopy
- FTIR: fourier transformation infrared
- HPLC: high performance liquid chromatography
- TEM: transmission electron microscopy
- TPR: temperature programmed reduction
- XPS: X-ray photoelectron spectroscopy
- XRD: X-ray diffraction
- UV-vis DRS: ultraviolet visible diffuse reflectance spectroscopy
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Chapter 1 Introduction and aims of this project

1.1 Introduction of this project
The engineering of porous materials, including microporous (pore size < 2nm), mesoporous (pore size 2 - 50nm (nanostructured materials)) and macroporous materials (pore size > 50nm), is emerging as a new area of great scientific and technological interest.

Prior to the discovery of this family of mesoporous materials, mesoporous materials were typically amorphous or para-crystalline solids, such as silicas [1], aluminas [2], modified layered materials and silicas [3-5]. However, the pores in these materials are generally irregularly spaced and broadly distributed in size [4]. MCM-41 [6], one of the members of the extensive family of mesoporous sieves, possesses a hexagonal array of mesopores varying approximately from 1.5nm to 10nm or even larger sizes. Therefore, the appearance of this family of mesoporous silica dramatically expanded the range of the crystallographically defined pore sizes from the micropore to the mesopore regime. Furthermore, the uniform and adjustable mesopore sizes can be easily enlarged to 30nm and even larger in some kinds of mesoporous silicas [7].

Unfortunately, mesoporous silicas possess neutral frameworks, which limit their applications in catalysis, and as molecular sieves, and adsorbents, etc. Therefore, functionalization of mesoporous silica is often necessary. There are two main methods for the synthesis of functionalized mesoporous silica: one is direct synthesis method, the other is post-synthesis method. In the direct synthesis method, functional species or their precursors are loaded during the synthesis of mesoporous silica. In contrast, via post synthesis method, functional species or their precursors are loaded into/onto mesoporous silica synthesized in advance. However, there are also some problems encountered in the synthesis of functionalized mesoporous silica. For example, for the direct synthesis method, it is difficult to load high amounts of functional species into the mesoporous silica frameworks. Blockage of mesopores often happens due to the
formation of bulk function guest species in the mesochannels when post synthesis method is employed. Such problems will be described by taking Ni and titania functionalized mesoporous silica as examples.

On the one hand, it is well known that supported nickel catalysts have been widely studied and used due to their very high activity in hydrogenation, hydrotreating and stream-reforming reactions [8]. Silica is the most commonly used nickel carrier. As above-mentioned, as far as mesoporous silica is concerned, uniformly hexagonal array of linear channels and mesostructures over long range make them very promising as catalyst supports. Therefore, combining as many catalytically active Ni species as possible with mesoporous silica is of great interest nowadays. Up to now, many nickel-containing mesoporous silicas were synthesized and tested in dimerization of ethylene and isomerization of butene [9], desulfurization of thiols and organic sulfides [10,11], deodorization [12] or hydrodechlorination [13] hydrogenation of benzene [14] and so on.

The most commonly used method to synthesize nickel-containing mesoporous silica is the impregnation method. The disadvantage of this method is that high loadings of nickel exceeding 5wt.% often leads to loss of the BET surface area or even blockage of mesochannels by large Ni particles. Therefore, an alternative way to introduce nickel species into the mesoporous silica, called direct synthesis method, is to add Ni salts, like NiCl₂, into the synthesis mixture, followed by the hydrothermal treatment. However, it is difficult to load high amounts of nickel. It is believed that rapid precipitation of nickel ions in basic conditions does not allow full interaction with the template molecules. This brings about low loading of nickel into the mesophases and formation of extra-framework NiO after calcination.

On the other hand, titania is the most studied photocatalyst system and has been found to be capable of decomposing various organics and inorganics in both liquid phase [15-17] and gas phase [18-20]. Nano-sized titania possesses greater surface area than
bulk titania and therefore greater amount of active surface sites. However, the nano-size TiO₂ particles usually used are very hard to recover after use. Silica-supported titania has been found to a good solution because it offers high active surface area and better recovery properties. Incorporation of titania into/onto microporous and mesoporous silica has been investigated extensively [21-26]. The blocking of the mesopores upon high titania content, however, often happens when the titania particles are formed in the mesochannels [24-26].

1.2 The aims of this project
This project intends to develop high loading Ni- and titania-functionalized mesoporous silica including their synthesis, characterisation and assessment of photocatalytic performance of TiO₂-containing mesoporous silica. The main aims are as follows.

Development of modified direct synthesis method
In order to increase the nickel loading into the mesoporous silica frameworks, a modified direct synthesis method will be developed. In this method, 'TEOS-seizing nickel species' co-hydrolyzes and co-condenses with TEOS during the hydrothermal treatment for building up mesostructures templated by the cationic surfactant.

Preparation and characterisation of nickel-containing mesoporous silica
In this section, the developed direct synthesis method will be examined for the incorporation of high amounts of nickel into the silica matrix. At the same time, the capability of this method in obtaining quality mesostructures will also be studied. Upon reduction, catalytically active nickel particles will be formed. Synthesized materials will be characterized by varieties of characterisation techniques, including the mesostructural ordering, nickel dispersion, surface area and porosity, chemical states and interactions of nickel with silica matrix, and nickel coordination..

Preparation and characterisation of titania-containing mesoporous silica
Chapter 1: Introduction and aims of this project

A new kind of post-synthesis method, called multi-incorporation method, will be developed to incorporate high amount of titania into mesoporous silica, SBA-15. In this method, titania will be incorporated not at a time but for more than one time to achieve the desired loading of titania into SBA-15. Using this method, it is expected that this method will afford no blockage of the mesopores. Synthesized materials will also be characterized by various characterisation techniques, including the mesostructural ordering, titania dispersion, crystallinity and particles size of titania phases, surface area and porosity, chemical states and interactions of titania phases with silica matrix. Additionally, photocatalytic performance of TiO\textsubscript{2}-containing mesoporous SBA-15 will be assessed.

Meanwhile, for comparison with functionalized mesoporous silica, mesoporous silica will be synthesized. MCM-41-type mesoporous silica with mesopore size of about 2.5nm and SBA-15-type mesoporous silica with mesoporous size of about 7.5nm will be prepared via the cationic surfactant templated route and block-copolymer templated route, respectively. Various characterisation techniques will be employed to examine the mesostructures.

A review of mesoporous materials and their applications will be included in chapter 2. Because the characterisation is a very important aspect for functionalized mesoporous materials, an independent chapter, number 3, was assigned not only to understand the mesostructures but also to investigate the functional species (Ni or TiO\textsubscript{2}). The following two chapters, number 4 and 5, are designed to present the results and discussion of nickel and titania-containing mesoporous silica, respectively.

References


Chapter 2 Reviews on mesoporous materials: synthesis and applications

2.1 Introduction

Since the discovery of the family of M41S in 1992 by Mobil scientists, mesoporous materials have attracted much interest [1, 2]. Before that, scientists have also developed a number of methods for the synthesis of porous materials (such as Zeolites) including utilizing small molecules as the templating agents, which can influence the shapes and pore sizes of the products aimed at achieving products with restricted pore size of about 1.5nm and very narrow pore size distributions [3]. However, the substantial extension of this approach to the synthesis of mesoporous silica was achieved by those chemists from Mobil. The key features of obtained mesoporous materials are the large specific surface area and orderly arranged mesopores in such silicas. They may act as excellent catalyst supports, on which active species can be highly dispersed. These materials are best known by their abbreviations such as MCM-41 and MCM-48 (MCM is the abbreviation of Mobil Composition of Matter, and 41 and 48 are just batch numbers). Various mesoporous silicas have since been synthesized and characterised, and their properties and applications been investigated. Based on these results, several possible formation mechanisms have also been proposed. In this chapter, the synthesis, including the formation mechanism proposed, and their application will be reviewed. Lastly, the existing problems and aims of this project will be discussed further.

2.2 Synthesis of mesoporous materials

2.2.1 Synthesis of mesoporous silica

The synthesis of mesoporous silica mostly involves the usage of inorganic precursors for building pore frameworks and surfactant serving as a template around which frameworks are built up, as shown in Figure 2.2.1. Removal of template leads to the formation of open mesostructures. Based on the surfactant used, typically, three kinds of mesoporous silica: (i) MCM-41, (ii) HMS (Hexagonal Mesoporous silica) and MSU series (MSU is the designation of mesoporous silica), and (iii) SBA-15 which were
synthesized using cationic, neutral, block-copolymer surfactants, respectively, will be introduced one by one.

![Schematic representation of the general synthesis process of mesoporous silica from organic surfactants and inorganic precursors.](image)

**Figure 2.2.1** Schematic representation of the general synthesis process of mesoporous silica from organic surfactants and inorganic precursors. In the synthesis mixture, the inorganic species (green dots) form the rigid mesostructures via the surfactant molecules-directed template process.

### 2.2.1 Ionic templating routes

Various pathways to the synthesis of such mesoporous materials have been developed not only for the silicas and aluminosilicas but also for other mesoporous non-silica materials. In fact, there is no better example than the synthesis of the mesoporous silicas, especially M41S for elucidating this templating process for synthesizing mesoporous materials [1, 2]. This route is based on the matching of anionic inorganic reagents and cationic surfactant cetyltrimethylammonium bromide ($CH_3(CH_2)_15N^+(CH_3)_3Br^-$, CTAB).

The inorganic precursors normally used are water glass and many silicon alkoxides (TEOS, TMOS etc) for the synthesis of mesoporous silica; and aluminium sulfate, alumina sodium aluminate, aluminium orthophosphate and aluminium acetylacetonate for the synthesis of mesoporous alumina [4]; and metal salts or alkoxides for the synthesis of corresponding mesoporous oxides such as mesoporous TiO$_2$ [5], and
mesoporous zirconia [6]. Here the focus is on the sol-gel process of TEOS, probably the most often used silica precursor.

The sol-gel process involves the generation of colloidal suspensions (‘sols’), which are subsequently converted to more viscous gels and thereafter to solids. The recent increased understanding of the underlying principles of this method has led to a great increase of interest in it and to its application in the production of a wide variety of advanced materials. There are two main processes occurring in the sol-gel process: hydrolysis and condensation, which will be introduced as follows taking tetraethyl orthosilicate (TEOS) as example.

**Hydrolysis:**

\[
Si(OEt)_4 + nH_2O \leftrightarrow Si(OEt)_{4-n}(OH)_n + nEtOH
\]

In hydrolysis, water plays an important role in the whole sol-gel process. In hydrolysis, although sometimes co-solvents (in this case, ethanol) are often added, water, in fact, serves not only as a solvent no matter how hydrophobic many precursors are, but also as one of the reactants. Hydrolysis leads to the formation of silanol groups Si-OH. During the hydrolysis, condensation may concurrently take place and can be represented as below:

**Condensation:**

\[
Si(OEt)_3OH + HOSi(OEt)_3 \leftrightarrow (EtO)_3Si-O-Si(OEt)_3 + H_2O (water- condensation)
\]

\[
Si(OEt)_3OEt + HOSi(OEt)_3 \leftrightarrow (EtO)_3Si-O-Si(OEt)_3 + EtOH (alcohol- condensation)
\]

Clearly, condensation will result in cross-linking among TEOS, partially or wholly hydrolysed TEOS, and partially condensed TEOS. As hydrolysis and condensation proceed, viscosity increases until the “sol” ceases to flow and form the “gel”. These two sol-gel processes for TEOS are water, pH, solvent, temperature, pressure etc. sensitive. It is worth noting that to form the solid, aging, drying and densification are also necessary. To make the silica solid possess mesoporous frameworks, the abovementioned hydrolysis and condensation processes require to be directed by template species, namely organic surfactants.
Therefore, the other important ingredient is organic surfactant, which serves as structure direct agents. For example, CTAB is one the most often used cationic template agent. Like other surfactants, it is a bi-functional molecule that contain a solvent-loving (lyophilic) head group and a solvent-hating (lyophobic) tail. As the result of amphiphilic nature, surfactants molecules can associate into superamolecular arrays for example in water.

CTAB in water will form spherical micelles that contain about 90 molecules. In the micelle, the hydrophilic head groups form the outer surface and the hydrophobic tails point toward the centre. It is because this arrangement minimizes the unfavourable interaction of the tails with water but introduces a competing unfavourable interaction, the repulsion of the charged head groups. These competing factors must strike the balance to ensure the stability of the micelles.

Figure 2.2.2 Schematic of phase diagram for CTMB in water [2b].

To illustrate the micellization of CTMB in water, liquid crystals phase (LCP) diagram is shown in Figure 2.2.2. It can be seen from this diagram that at very low concentration, the surfactant exists as single molecules dissolved in solution and absorbed at interfaces. At slightly higher concentration, called CMC1 (CMC is the abbreviation of critical micelle concentration) in the diagram, micelles are present. At
CMC2, cylindrical micelles can form. Following an increase of concentration, the hexagonal packed phase is attained, followed by the formation of cubic phase and lamellar liquid crystal phase. At very high concentration, the inverse phase in which water is solvated at the interior of the micelles, and the head groups point inward can be obtained. For the synthesis of mesoporous silica, the concentration of CTAB in water is often less than CMC2. The resemblances between hexagonal LCP structures formed by rod-like micelles with MCM-41 mesostructures, and the cubic LCP structure with MCM-48, lead scientists to propose a LCP mechanism for the formation of mesoporous silica.

After adding the inorganic species into the water solution of CTAB, the mixtures are adjusted to proper pH values and then allowed to react at relatively high temperatures (70-150°C) for several hours or longer. The resultant solids are washed, dried and then calcined at higher temperatures for selected time to burn off the organic templates (sometimes, template can also be extracted by means of repeated washing with slight acidified mixtures of organic solvent and water). Long-range ordered mesostructures will be obtained as shown in Figure 2.2.3a. The darker areas represent walls, between which there are mesopores.

Figure 2.2.3 Transmission electron micrographs of several MCM-41 materials having average pore sizes of (a) 20, (b) 40, (c) 65, and (d) 100Å [2a].
Table 2.2.1 Effect of surfactant chain length on MCM-41 pore size XRD d$_{100}$ peak location, hexagonal unit cell parameters [2a]

<table>
<thead>
<tr>
<th>Surfactant chain length $C_nH_{2n+1}(CH_3)N^+$</th>
<th>XRD d$_{100}$ spacing (Å)</th>
<th>$a_0$ (Å)</th>
<th>Ar pore size (Å)</th>
<th>Total benzene uptake (wt %) at 50 Torr</th>
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<td>Siliceous Products</td>
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<td>45</td>
<td>38</td>
<td>61</td>
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</table>

*$a_0 = 2d_{100}/\sqrt{3}$.

Some modifications to the synthesis procedure for mesoporous silica described above are often carried out, for example, to engineer the pore size. Some cationic surfactants with shorter or longer hydrophobic chains can lead to different mesopore sizes. The relation of chain length with mesopore size is described in Table 2.2.1. The pore diameter increases with increasing surfactant chain length. Additionally, increase in total benzene uptake was found with increasing surfactant chain length [2a].

Table 2.2.2 Effects of amount of mesitylene (TMB) on pore size of MCM-41 [2a].

<table>
<thead>
<tr>
<th>TMB added (g)</th>
<th>0</th>
<th>6</th>
<th>9</th>
<th>22</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average pore size (Å)</td>
<td>40</td>
<td>45</td>
<td>50</td>
<td>65</td>
</tr>
</tbody>
</table>

The auxiliary organics also have great influence on the pore sizes (see Table 2.2.2). They may encapsulate and swell the organic phase of inorganic-organic composites to increase the pore sizes [2a]. These materials, however, display somewhat irregular, yet essentially preserved hexagonal shape (shown in Figure 2.2.3, b, c, and d).

Undoubtedly, through approaches other than the combination of cationic surfactant and anionic inorganic precursor, like the use of the anionic surfactants [5, 7], or
Gemini surfactant [5, 6], mesoporous silica can also be prepared. The basic strategy is almost the same: surfactant-assisted build-up mesostructures.

### 2.2.1.2 Neutral approaches

The neutral templating ($N^{010}$) pathway for preparing the mesoporous molecular sieves is demonstrated to be based on the hydrogen bonding interactions. Now, the specific approaches to synthesis of such materials need to be described.

**Table 2.2.3 Physicochemical properties of MSU silicas and MSU alumina synthesized via $N^{010}$ approach.**

<table>
<thead>
<tr>
<th>Material designation</th>
<th>Template</th>
<th>surfactant</th>
<th>concentration mol/L</th>
<th>Abrev. formulation</th>
<th>d$_{100}$ (nm)</th>
<th>HK pore diameter/nm</th>
<th>BET S.S.A $m^2/g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSU-1</td>
<td></td>
<td>T15-S-9</td>
<td>0.1</td>
<td>C$_{11-15}$(EO)$_9$</td>
<td>5.2</td>
<td>2.5</td>
<td>1010</td>
</tr>
<tr>
<td>silica</td>
<td></td>
<td>T15-S-12</td>
<td>0.1</td>
<td>C$<em>{11-15}$(EO)$</em>{12}$</td>
<td>4.1</td>
<td>3.1</td>
<td>1005</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T15-S-15</td>
<td>0.1</td>
<td>C$<em>{11-15}$(EO)$</em>{15}$</td>
<td>5.4</td>
<td>2.6</td>
<td>640</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T15-S-20</td>
<td>0.1</td>
<td>C$<em>{11-15}$(EO)$</em>{20}$</td>
<td>7.8</td>
<td>4.8</td>
<td>605</td>
</tr>
<tr>
<td>MSU-2</td>
<td></td>
<td>TX-114</td>
<td>0.023</td>
<td>C$_8$Ph(EO)$_8$</td>
<td>6.1</td>
<td>2.0</td>
<td>780</td>
</tr>
<tr>
<td>silica</td>
<td></td>
<td>TX-100</td>
<td>0.027</td>
<td>C$<em>8$Ph(EO)$</em>{10}$</td>
<td>6.2</td>
<td>3.5</td>
<td>715</td>
</tr>
<tr>
<td>MSU-3</td>
<td></td>
<td>P64L</td>
<td>0.054</td>
<td>PEO$<em>{13}$PPO$</em>{30}$PEO$_{13}$</td>
<td>6.1</td>
<td>5.8</td>
<td>1190</td>
</tr>
<tr>
<td>silica</td>
<td>Ti(5%)-NTS</td>
<td>T15-S-12</td>
<td>0.08</td>
<td>C$<em>{11-15}$(EO)$</em>{12}$</td>
<td>4.9</td>
<td>3.0</td>
<td>950</td>
</tr>
<tr>
<td>Ti-MGU-1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>silica</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MSU-3</td>
<td></td>
<td>P64L</td>
<td>0.012</td>
<td>PEO$<em>{13}$PPO$</em>{30}$PEO$_{13}$</td>
<td>6.3</td>
<td>4.8</td>
<td>420</td>
</tr>
</tbody>
</table>

* The X-ray reflections are quoted for materials calcined in air at 873K. Framework-confined mesopore sizes were determined by HK analysis [11] of $N_2$ adsorption isotherms, and surface areas were determined by BET method [10].
Figure 2.2.4 TEM photograph of MSU-1 [10].

For example, Tanev et al [8, 9] have prepared the hexagonal mesoporous silica (HMS) and Ti-HMS with molar ratio of Ti:Si=1:100 using the dodecylamine (DDA) as a template. Another approach (N0T0) using the non-ionic polyethylene oxide surfactants as structure-directing agent has been used by Bagshaw et al [10], and other scientists [12] to synthesize the hexagonal mesoporous silica. The mesopore sizes and other physicochemical properties of the products from different surfactants are shown in the Table 2.2.3. TEM in Figure 2.2.4 shows that such materials lack long-range ordering. In fact, only disordered, hexagonal-like packing of channels in MSU-1 is seen.

With many advantages of using neutral templating agents, this approach overcomes drawbacks of neutral alkyamines, such as its high toxicity and high price. The surfactants used are low-cost and especially environmentally compatible, and make themselves exceptionally promising neutral templating agents. Additionally, many achievements have been gained via another approach, such as block copolymers templating methods.

2.2.1.3 Block copolymers templating methods

Tri-block copolymers can also be utilized as structure-directing agents for the synthesis of mesoporous materials. Zhao et al [13, 14] have prepared mesoporous silica with periodic and adjustable pore from 5.0 to 30.0nm (see Figure 2.2.5).
Figure 2.2.5 TEM images of calcined hexagonal mesoporous silica prepared using tri-block \( \text{PEO}_{20} \text{-PPO}_{70} \text{-PEO}_{20} \) with various mean pore sizes: (A) 6.0nm, (B) 8.9nm, (C) 20.0nm, (D) 26.0nm [13].

Using acidic (pH≈1) aqueous conditions, 2-d hexagonally ordered mesoporous materials, SBA-15, with thicker walls and long-range regular mesochannels can be synthesized. Typically, preparation of SBA-15 using tri-block \( \text{PEO}_{20} \text{-PPO}_{70} \text{-PEO}_{20} \) (poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) block copolymers) as structure-directing agents was carried out at temperatures ranging from 35 to 80. After moderate stirring at low temperatures at 35–80, hydrothermal treatment is necessary for obtaining mesostructures of good quality [13].

\( \text{N}_2 \) adsorption-desorption isotherm of SBA-15 exhibits type IV nitrogen physisorption curve and \( \text{H}_1 \)-type hysteresis loops, which are characteristic of unique capillary condensation due to the mesoporous structure. A clear \( \text{H}_1 \)-type hysteresis loop is observed and the condensation occurs at \( p/p^0 = 0.6 \). All of these demonstrate the existence of the mesopores in SBA-15 [13].

This synthesis method has many advantages:
(a) Adjustable pore sizes and thickness of silica walls by varying heating temperature (35-140°C) and time (11-72 hours).

(b) A broad range of the reaction mixture compositions and the conditions.
Templating agents: 0.5-6wt%, temperatures: 35 -80 , and the pH values: not higher than 1.

(c) No selectivity for the acid—HCl, HBr, HI, H2SO4, H3PO4.

(d) High regularity of the pores.

(e) High hydrothermal stability of calcined mesoporous silica SBA-15 than MCM-41.

The structure-directed assembly of mesoscopically ordered silica by dilute poly(alkylene oxide) tri-block copolymers in acid media likely occurs by a pathway that involves a combination of the electrostatic and hydrogen bonding interactions. Under acidic conditions, the PPO block is more hydrophobic than the PEO block in temperature range of 35°C- 80°C [13, 15], thereby increasing the tendency for the mesoscopic ordering to occur. At pH ≈ 1, positively charged protonated silicate species interact preferentially with the more hydrophilic PEO blocks to promote cooperative assembly of a silica-block copolymers-rich mesophase from a dilute water-rich phase. Concurrent and further condensation of the silica species in the presence of the block copolymer surfactant species result in the formation of mesophase silica composite.

Yang et al [16] also prepared many mesoporous metal oxides using the poly (alkylene oxide) tri-block copolymers as shown Figure 2.2.6. From the TEMs recorded along the 001 axis, it can be seen that, in mesoporous SnO2, ZrO2 and SiAlOy, the mesoscopically ordered channels can be clearly observed.
2.2.2 Mechanisms of mesostructures formation

Since the discovery of mesoporous silica, the mechanism responsible for the formation of MCM-41 from its precursors has attracted much attention. There are many models proposed to interpret the formation of mesostructures and to provide a basis for engineering various mesoporous materials, including synthesis, characterisation, functionalization, etc. These models involve sophisticated interactions between the organic surfactant molecules and the inorganic species. The resultant organic-inorganic mesostructures can be regarded as a hexagonal array of surfactant micellar rods embedded in a silica matrix. Subsequent removal of the surfactants leads to the formation of open mesostructures.

2.2.2.1 Liquid crystal templating mechanism
One of the proposed mechanisms is the ‘liquid crystal templating’ (LCT) mechanism, which was proposed by the Mobil researchers in 1992 and is based on the resemblances between liquid crystalline surfactant assemblies and MCM-41 [2, 3]. MCM-41 with hexagonally packed cylindrical mesopores is one of the most representative mesoporous silicas. Based on the synthesis of MCM-41-type mesoporous silica, two mechanistic pathways were given by the Mobil researchers, as shown in Figure 2.2.7 and discussed as follows.

(1) Liquid crystal mesophases may form prior to the addition of silicate species. The aluminosilicate precursor species, or pure silica species occupy the space between a preexisting hexagonal lyotropic liquid crystal (LC) phase and deposit on the micellar rods of the LC phase (pathway 1 in Figure 2.2.7); (2) the silicate species added to the reaction mixture may influence or direct the ordering of the isotropic rod-like micelles to the desired liquid crystal phase, i.e., hexagonal mesophases. Therefore, the mesophases formed are directed by the existing liquid crystal micelles structurally and morphologically (pathway 2 in Figure 2.2.7).

**Figure 2.2.7** Schematic model of liquid crystal templating mechanism via two possible pathways [2, 3]: (1) is liquid crystal initiated and (2) is silicate anion initiated.

The influence of alkyl chain length and the addition of mesitylene (TMB) on the pore size have been taken as strong evidence for the LCT mechanism (pathway 1), since this phenomenon is very consistent with the well-documented surfactant chemistry [15, 17].
Additionally, the auxiliary organic species added to the reaction gel can be solubilised inside the hydrophobic regions of micelles, causing an increase in micelle diameter which results in the increase of the pore size of MCM-41. The LCT mechanism (pathway 1) has been further confirmed by many subsequent reports [18-20].

However, mesoporous silica can also be synthesized without the presence of LC. It is reported that no hexagonal liquid crystalline mesophases were found either in the synthesis gel or in the surfactant solution used as a template [18, 21]. It was, therefore, assumed that formation of MCM-41 phase is possibly via pathway 2 rather than the pathway 1. In this alternative mechanism, the rod-like micelles assemble not prior to but during the formation of MCM-41 mesostructures. Specifically, it is the interactions between randomly ordered rod-like micelles and silicate species in the reaction mixture that lead to approximately two or three monolayers of silicate encapsulation around the external surfaces of the micelles. These randomly ordered composite species spontaneously pack into a highly ordered mesoporous phase with an energetically favourable hexagonal arrangement, which minimizes the electrostatic repulsions between charged surfaces of micelles accompanied by silicate condensation. With increasing heating time, the inorganic wall continues to condense.

### 2.2.2.2 Cooperative templating mechanism

Other than the LCT mechanism, a cooperative templating mechanism for the formation of mesoporous materials based on the specific type of electrostatic interaction between a given inorganic precursor \( I \) and surfactant head group \( S \), was proposed by Huo and co-workers [5, 7]. Extension has been achieved from the \( S^+I^- \) pathway in the LCT mechanism (Figure 2.2.7). This pathway involves the use of anionic silicate species, \( I^- \), and cationic quaternary ammonium surfactant, \( S^+ \). Other charge-interaction pathways are \( ST^+, S^+IT^+, ST^+XIT^+ \), and hydrogen bonding: \( S^0I^0 \) and \( N^0I^0 \) pathways. \( M \) is a metal cation, \( X \) is halide anion. This categorization is useful, especially when other types of inorganic-organic interactions are considered. As shown in Figure 2.2.8, six kinds of inorganic-organic interactions were listed.
Figure 2.2.8 Schematic representation of the various types of inorganic-surfactant head group interactions: electrostatic: a) $S^+I^-$, b) $S^-I^+$, c) $S^+ICI^+$, and d) $S^-Ni^+$; hydrogen bonding: e) $SO_{10}$ and f) $NO_{10}$.

The success of the cooperative templating mechanism is illustrated in Figure 2.2.9 by the diverse compositions of organic-inorganic mesostructures. From this figure, it can be seen that: a) Single-chain surfactant molecules react preferentially with silicate polyanions (e.g. dimers, double three and four rings) which displace the original surfactants monoanions. Micelles serve as a surfactant molecule source or are rearranged according to the anion charge density and shape requirements; b) and c) Nucleation and rapid precipitation of organized arrays takes place with configurations determined by the cooperative interactions of ion-pair charges, geometries and organic van der Waals forces. Silicate condensation at this stage at low temperatures is minimal. d) Condensation of the silicate phases takes place. The silicate framework charge decreases during this process and may lead to liquid-crystal-like phase transitions as the surfactant phase tries to reorganize the changing interface charge density [5].
Therefore, a possible $S^+X^-T^+$ pathway related to the cooperative templating mechanism has been proposed [5, 7]. By operating below the iso-electric point of silica (pH~2) under acidic conditions, the silicate species were cationic ($I^+$). The same ammonium surfactant $S^+$ could be used as a templating agent but the halide counter-anion $X^-$ became involved through this pathway as it served to buffer the repulsion between the $I^+$ and $S^+$ by means of weak hydrogen-bonding forces.

2.2.2.3 Transformation mechanisms

Another formation mechanism is the transformation from lamellar to hexagonal mesophases. There are four models describing such transformation: assembly of silicate rod [18], silicate layer puckering [21], ‘charge density matching’ [22, 23], and
‘folding sheets’ [24-26].

Figure 2.2.10 Schematic for assembly of silicate rods model.

2.2.2.3.1 Assembly of silicate rods

By carrying out in situ $^{14}$N NMR spectroscopy, Davis et al. [18] concluded that the liquid crystalline phase does not exist in the synthesis medium during the formation of MCM-41. They, therefore, concluded that this phase could not be the structure-directing agent for the synthesis of the mesoporous material in agreement with the already proposed mechanism through pathway 2 shown in Figure 2.2.7. Thus, as shown in Figure 2.2.10, they propose that the randomly ordered rod-like organic micelles interact with silicate species to yield two or three monolayers of silica around the external surface of the micelles. Subsequently, these composite species spontaneously condense into the long-range ordered mesostructures characteristic of MCM-41 in order to alleviate the repulsive electrostatic interactions of silicate species. If one wants to remove the surfactant by calcination, just at the point when the long-range order is achieved, i.e. short synthesis times, the material will not be stable as a consequence of the still large number of non-condensed silicate species. Longer synthesis time and/or higher temperature can increase the degree of condensation of silicate species giving as a result stable materials. The model described above operates under a wide range of synthesis conditions, such as gel composition, pH, timescale, temperature and pressure.
2.2.2.3.2 Silicate layer puckering

As shown in Figure 2.2.11, instead of the formation of silicate-covered micellar rods, Steel et al. [21] postulated that surfactant molecules could assemble directly into the hexagonal LC phase upon addition of the silicate species, based on $^{14}$N NMR spectroscopy. From this figure, it can be seen that the silicates were organized into layers, with rows of the cylindrical rods intercalated between the layers. Aging the mixture caused the layers to pucker and collapse around the rods, which then transformed into the surfactant-containing MCM-41 hexagonal-phase mesostructures.

2.2.2.3.3 'Charge density matching'

Figure 2.2.12 Schematic for ‘Charge density matching’ model.
Another model (Figure 2.2.12) was presented by Monnier et al. [22, 23] to explain the formation and morphologies of silicate-surfactant mesostructures. Transformation from the lamellar to hexagonal mesophases was confirmed evidenced by XRD results, see Figure 2.2.13. Initially precipitated layered materials with lamellar mesophases (line A in Figure 2.2.13) evolved into hexagonal mesostructures (line C in Figure 2.2.13) after hydrothermal treatment for a long period of time. It was found that the oligomeric silica polyanions can easily act as multidentate ligands, which have sufficiently high charge density and can strongly interact with cationic head groups of surfactant in the silicate-surfactant interfaces. Preferential polymerization of these silicate oligomers leads to an increase in interfacial area that is achieved through corrugation of the lamellar silicate-surfactant sheets. As polymerization proceeds, diminished charge density of larger silica polyanions leads to the increase in the average head-group area of the surfactant assembly. This increase will drive the transformation of lamellar mesophases into hexagonal mesophases in order to maintain the charge density balance between the silica polyanions and head groups of surfactant.

2.2.2.3.4 Folding sheets’
The lamellar-to-hexagonal phase transformation also appeared in materials, which were prepared from the intercalation of the ammonium surfactant in kanemite, a type of hydrated sodium silicate composed of single-layered silica sheets [24-26]. Figure 2.2.14 shows the schematic for this lamellar-to-hexagonal phase transformation. From this figure, it can be seen that sodium ions are present for charge-compensating between these silica layers. After the surfactants are ion-exchanged into the layered structure, it is believed that the silicate sheets will fold around the surfactants and condense into a hexagonal mesostructures. The final product is very similar to MCM-41.
2.2.3 Functionalization of mesoporous silica

As mentioned previously, since the discovery of the family of M41S in 1992 by Mobil scientists, the synthesis of mesoporous materials have attracted much interest. However, the siliceous MCM-41 is of limited use as catalysts due to lack of acidic sites or ion-exchange capacity. These days, the functionalization of mesoporous silica will no doubt result in products with versatile application in many fields. Therefore, the success achieved in preparing silica was the starting point for using the concept to produce functionalized mesoporous silica. To create catalytic active sites, many non-silicon elements have been incorporated into/onto the mesopores of mesoporous silica, such as Al, Ga, Mn, V, Cr, Fe, Zr, Ti, B and so on. In this chapter, synthesis of Al, Ti, Ni-functionalized mesoporous silica will be discussed in detail, because Al is the most investigated element that was directly incorporated into mesoporous silica, it may help to elucidate the direct synthesis method.

There are two basic methods of loading active sites onto/into mesoporous silica, namely the direct synthesis and post-synthesis methods. The former refers to the direct incorporation of the active species or their precursors into the synthesis gel of mesoporous silica. After hydrothermal treatment and calcination, active sites will be loaded into or partly into the silica walls. The active species loaded are normally of limited amount with the aim of obtaining good mesostructures. As for the post-synthesis method, such as the ion-exchange method, impregnation method, active species were loaded into synthesized mesoporous silicas. This method, although it can result in a high amount of loading, often cause other problems, such as the blockage of the mesopores due to the growth of guest particles upon high loading. All of these will be discussed in detail below.

2.2.3.1. Direct synthesis method

Due to the demands of acid-catalyzed reactions, Al-containing mesoporous (Al-M41s) silicas, one of the most often synthesized functionalized mesoporous silicas, have been patented [27-29], extensively reviewed [30-33] and published in open literature [1 2,
4, 8, 34-47]. Al-MCM-41s were prepared under hydrothermal conditions, typically at 70-150 °C for 1~10 days. Various sources of silica were used, including HiSil, Ultrasil, Cab-O-Sil, tetramethylammonium silicate, tetraethyl orthosilicate, and sodium silicate [2]. Likewise, a large number of aluminium sources were used. The list of such sources includes Catapal B alumina [2, 4, 36], sodium aluminate [2, 4, 37-39], aluminium nitrate [46], aluminium sulfate [4], aluminium isopropoxide [46], aluminosilicate [43, 44].

As for the best aluminium source for the preparation of aluminium-rich MCM-41, different workers have reached different conclusions. Janicke et al. [36] reported that Al-containing MCM-41s with Si/Al ratios down to 16 could be obtained using aluminium isopropoxide as the aluminium precursor other than Catapal B, with aluminium being incorporated entirely in tetrahedral coordination. Luan et al. [4] found that almost all Al in the final material was six-coordinated and did not belong to the silicate frameworks when Catapal alumina or sodium aluminate was used. Aluminium sulfate led to total incorporation of Al in tetrahedral sites up to very high loadings (Si/Al=2.5). On the contrary, Schmidt et al. [37, 38] and Borade and Clearfield [39] prepared Al-rich samples using sodium aluminate. Fu et al. [43, 44] prepared MCM-41 aluminosilicates using a two-step approach. Instead of using gel precursors followed by hydrothermal crystallization, they first prepared well-defined aluminosilicate oligomers to be used as precursors. In a second step, these precursors were precipitated with the presence of surfactant and then treated with water vapour at 383K for 3 days. This method not only affords MCM-41 aluminosilicates with variable Si/Al ratios down to the lowest possible ratio of 1/1 but also offers additional flexibility in the design of new materials by using suitable building blocks.

Incorporation of aluminium in the mesostructures results in a noticeable decrease in the intensity and significant loss of resolution of high-angle diffraction peaks [4, 39]. Broadening of the pore size distributions was often observed [44].
Table 2.2.4 Structural parameters of Al-MCM-41 [31]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si/Al ratio</th>
<th>Gel</th>
<th>Product</th>
<th>d_{100} spacing (Å)</th>
<th>S_{BET} (m²/g)</th>
<th>Pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-MCM-41</td>
<td>100</td>
<td>34.0</td>
<td>1340</td>
<td>1.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-MCM-41-100</td>
<td>50</td>
<td>35.5</td>
<td>1447</td>
<td>1.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-MCM-41-50</td>
<td>25</td>
<td>35.5</td>
<td>1441</td>
<td>1.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-MCM-41-25</td>
<td>10</td>
<td>35.5</td>
<td>1465</td>
<td>1.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-MCM-41-10</td>
<td>5</td>
<td>35.5</td>
<td>1318</td>
<td>1.24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-MCM-41-5</td>
<td>2</td>
<td>35.5</td>
<td>823</td>
<td>0.75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-MCM-41-2</td>
<td>2</td>
<td>35.5</td>
<td>132</td>
<td>0.18</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

BET surface area decreases sharply when Si/Al drops down from 5 to 2, as shown in Table 2.2.4, indicating the collapse of mesostructures.

Since Perego et al. [48] reported on the remarkable selective oxidation properties of Ti-modified silicalite-1 (TS-1), the field of transition-metal-modified zeolites has grown tremendously. These catalysts were found to be highly effective in the oxidation of a large number of organic substrates into valuable chemicals in the presence of dilute H₂O₂ under modest conditions. The titanium-modified mesoporous silicates have been reported in the patent literature [49].

Many groups have reported independently on the synthesis and characterization of Ti-MCM-41[50-52] and Ti-HMS [8]. Corma et al. [50, 53] prepared Ti-MCM-41 under hydrothermal conditions (413 K, 28 h). They used silica sources, such as, fumed Aerosil silica, and Ti alkoxides as Ti sources. Cetyltrimethylammonium bromide/hydroxide was used as surfactant. Similar catalyst preparations were also used by other workers [51, 52, 54]. Pinnavaia et al. [8, 55] prepared the so-called Ti-HMS, where HMS stands for hexagonal mesoporous silicate. The main difference between the preparation methods for MCM-41 and for HMS materials is that the latter is synthesized in the presence of long-chain primary amines instead of charged surfactants. Additionally, non-ionic polyethylene oxide was used as template to synthesize Ti-containing mesoporous silica (Ti-MSU-1) [10]. A tri-block polymer, P123 (poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide)) served as a structure-directing agent for the synthesis of Ti-mesoporous silica under extremely
acid condition [56-57]. Newalkar et al. [56] reported the synthesis of Ti-SBA-15 via a direct synthesis method under microwave conditions using P123. Similarly, Zhang et al. [57] reported a new approach to synthesize Ti-substitute SBA-15. NH₄F, which was employed to accelerate the hydrolysis of tetramethyloxysilane, plays an important role in forming Ti-SBA-15 of high quality. It has been shown that procedures and strategy for the synthesis of Ti-mesoporous silica are similar to those for pure mesoporous silica [13, 14].

All XRD patterns of Ti-containing samples are dominated by a peak at 2θ < 3° corresponding to the 100 diffraction. Depending on the preparation processes, the Ti-MCM-41 samples possibly have weaker 110, 200, and 210 reflections in the 2θ range of 4-7°. HMS-based catalysts exhibited only the 100 diffraction peak, even though, according to Tanev et al. [8], they displayed electron diffraction patterns characteristic of hexagonal structure. However, for Ti-SBA-15, with increasing amount of Ti incorporated, the mesostructures did deteriorate [57].

There are few reports that concern nickel-containing mesoporous silicas via direct synthesis method (DS method). Hartmann et al. [58] reported the synthesis of Ni-MCM-41 in their work. A little amount of NiCl₂ was introduced into the synthesis gel, in which cetyltrimethylammonium chloride (CTAC) was used as the template. As reported by Parvulescu et al. [59], Ni-MCM-41 was synthesized by hydrothermal treatment. Typically, the corresponding quantity of the nickel salt (Ni(CH₃COO)₂·4H₂O) in aqueous solution was added to a mixture of sodium silicate, CTMB and H₂O under stirring. After 2 h of stirring, TMAOH solution was added. The pH value of the gel was adjusted to 11 with H₂SO₄. The gel obtained was sealed into Teflon-lined steel autoclaves and heated for 5 days at 373 K. The solid products were recovered by filtration, washed and dried in air. The as-synthesized samples were calcined at 773K in a flow of N₂ followed by air. It is apparently difficult to load a high amount of nickel without damaging the mesostructures by using the DS method. Therefore, to heighten the nickel loading into the mesoporous silica via this method is
one of our aims in this project and will be discussed in chapter 4 in great detail.

Additionally, other hetero-elements, such as V [60-72], Cr [70, 73, 74], Mn [60, 75-76], Fe [45, 59, 77-78], Co [59, 79], B [80-84], Ga [45, 85, 86], can also be incorporated into the silica walls via the DS method.

### 2.2.3.2 Post-synthesis method

Pre-synthesized mesoporous silica can be used as a support for active species. Normally, the functionalization process performed is a post-synthetic procedure, such as the ion-exchange and impregnation methods. The ion-exchange method is only confined to pickup little amount of active species, while the impregnation method can lead to relatively high loading. Here, articles that concern titanium and nickel-containing mesoporous silicas synthesized via post-synthesis method, including their synthesis, characterization and acknowledged applications will be reviewed.

The catalytic activity of Ti(IV) framework-substituted microporous materials, e.g., TS-1 and TS-2 [48] is somewhat limited by the fact that only those small reactants can gain access to the Ti centers through channels of zeolites. This prevents their use in areas where bulkier reactants dominates. Loading the titania in forms of either isolated Ti(IV) species or small titania nanoparticles have made these catalysts much more attractive and applicable.

Maschmeyer et al. [87, 88] have described a method of introducing Ti(IV) ions onto the framework of MCM-41 silicas using titanocene dichloride as a precursor. Ti-containing MCM-41 becomes an active catalyst for selective oxidation of even bulky substrates with a large number of accessible Ti sites offering the potential of shape selectivity through the structure of the mesoporous frameworks. They found that after calcination, the dominant surface Ti species is the ($\equiv$SiO)$_3$TiOH complex with appreciable concentrations of ($\equiv$SiO)$_3$Ti(OH)$_2$ species.
Similarly, Zheng et al. [89] used tetra butyltitanate (TBOT) as Ti source for the synthesis of Ti-containing MCM-41. The synthesis procedure can be schematically represented by Figure 2.2.15. It can be seen from this figure that synthesized MCM-41 was impregnated with the appropriate amount of TBOT in hexane. After hydrolyzation and calcination, titanium species could be anchored on the walls of the mesoporous silica.

Well-dispersed titania \((\text{TiO}_2)_n\) \((n=30-70)\) clusters can be attached to the silica walls of MCM-41 [90]. It is worth noting that the starting material, as-synthesized MCM-41, was used for the impregnation of TiCl\(_4\) in hexane. Using the post-synthesis method, Morey et al. [91] reported that titanium species could be loaded into MCM-48. Comparing SBA-15 with MCM-41-supported titania particles, Grieken et al. [92] concluded that SBA-15 was more stable than MCM-41 upon the loading of titania and titania particles size was controlled in the range of 6~10nm. Belhekar et al. [93] reported synthesis of titania-containing HMS via the impregnation of TBOT in isopropyl alcohol. Titania (25wt%) containing mesoporous silica was also synthesized using the requisite amount of TTIP in the iso-propanol [94].
Loading a high amount of titania at a time into the mesochannels (called the one step impregnation method, designated as the OSI method) often leads to the blockage of mesopores due to the formation of large titania particles [92, 93]. This is the main problem from which OSI method suffers. More details and our solution to this problem will be given in chapter 5.

Similarly, via the post-synthesis method, nickel can also be incorporated into/onto the mesoporous silica. Through the impregnation method, Ziolek et al. [95] have incorporated nickel into mesoporous silica using nickel nitrate as the precursor salt. Additionally, MCM-41-supported nickel (3wt% nickel) catalysts were synthesized, and their catalytic activity in hydrogenation of benzene was examined [96]. NiMo supported on MCM-41 was proven to be able to afford superior catalytic activities to amorphous silica-alumina and USY zeolite-supported Ni/Mo [97] (USY, the name of one kind of zeolite). Using nickel nitrate as a nickel source, (P)NiW and (P)NiMo-containing Ti-HMS was synthesized with nickel oxide content of 3.17 and 3.44 wt.% [98]. Disordered mesoporous KIT-1 can also be used as the support for nickel. As reported by Yue et al [99], using the impregnation method (nickel nitrate as nickel source), NiO tends to forin small crystallites in the mesoporous channels. Rodríguez-Castellón et al. [100] reported the synthesis and characterization of catalysts with nickel (14.9 and 28.7 wt.% Ni) supported on a Zr-doped mesoporous silica (Si/Zr molar ratio of 5) via a similar post-synthesis method (nickel nitrate as nickel source). Up to 5wt.% nickel can also be loaded into MCM-41 and AIMCM-41 using the ion-exchange or impregnation method. It is worth noting that, even with low nickel content (1.7wt.%), bigger nickel particles (mean particle size of about 13nm) were visible [101] as seen in Figure 2.2.16(left). As shown in Figure 2.2.16(right), 1-2nm nickel particles were also observed on AIMCM-41-supported nickel (1.48wt.%) catalysts synthesized by the ion-exchange method [102].
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Figure 2.2.16 TEM of MCM-41 (left, in Ref.[101]) and AIMCM-41(right, in Ref.[102])-supported nickel catalysts.

It was reported that Ni-boride, with nickel content up to 10.6wt.%, catalyst was synthesized by low-temperature reduction of surface-adsorbed nickel chloride with ethanolic sodium borohydride solution in order to overcome the shortcoming that MCM-41 is not stable in basic medium. That using nickel citrate instead of nickel nitrate can improve the dispersion of nickel on the porous silicas has been reported [104, 105]. Finely dispersed nickel particles supported on SBA-15 was prepared by grafting EDTA onto the SBA-15 surface to grasp the Ni (II) ions, which were transformed into nickel after calcination at 400 [106].

Although there are many reports dealing with combining mesoporous silica and catalytic active nickel via the post-synthesis method, blockage of mesopores due to the presence of bulk guest nickel species (Ni\(^0\) or NiO) even upon low loading often occurs as abovementioned. This is the reason why the DS method (section 2.2.3.1) was used instead of the post-synthesis method.
2.2.3.3 Synthesis of mesoporous non-silica materials

Since the discovery of mesoporous silica, much effort has been devoted not only to the synthesis of functionalized mesoporous silica, but also to the preparation of mesoporous transition metal oxide (MTMO) due to their great potential in the fields of electromagnetics, photoelectronics, catalysis and separation [107 108].

![Diagram of synthesis pathways](image)

Figure 2.2.17 Schematic representation of four pathways to create mesoporous or mesostructured materials [108].

The strategy for the synthesis of these non-siliceous MTMO is either quite similar to those for mesoporous silica or involving the use of mesoporous silica except for the
'nanocrystal templating' as shown in Figure 2.2.17. There are several pathways leading to the formation of MTMO. As to the above two, they both have been proved to be successful for the synthesis of mesoporous silica. The formation mechanism of mesoporous silica was introduced in section 2.2.1. For the 'nanocasting' pathway, using the mesoporous silica as the mold to template the formation of non-siliceous MTMO or other materials was also reported. 'Nanocrystal templating' pathway often leads to the formation of disordered pore system. The focus of this section is on introducing the evolution of the synthesis of mesoporous titania and NiO. A brief overview for other non-siliceous MTMO or other mesoporous materials will also be given here.

2.2.3.3.1 Mesoporous titania

Due to the photocatalytic activity in the degradation of organic pollutants in water and the success in the synthesis and wide applications of titania-supported on mesoporous silica, mesoporous titania has drawn the interest of many researchers.

In 1995 Antonelli and coworkers first synthesized mesoporous titania by using phosphate as template [109]. The use of complex Ti(OR)_{4-x}(acac)_x (acac, acetylacetonate) precursors, combined with phosphonate anionic surfactants in slightly acid medium (pH 3-6), led to the first documented titania-based mesoporous oxide, TMS-1. However, it was not pure titania, and phosphorus was bound strongly to the molecular sieve. [110-111]. Putnam et al. [110], on the basis of XRD and TEM studies, claimed that the TMS-1 phase exists only as a minor component of a larger lamellar mesostructured solid, in such a way that the whole material should have low surface area (47–63 m^2g^-1). In contrast, Stone and Davis [111], who used the same preparative procedure, again reported on mesoporous solids having high surface areas (600–700 m^2g^-1) after calcination at moderate temperature (230°C). Unfortunately, in all these reports, it was also noticed that a significant amount of phosphate remained in the calcined materials (e.g. P:Ti molar ratio in the range of 0.57–0.68:1), with the subsequent poisoning of the surface catalytic sites [111]. Nonionic amine templates
have been employed to avoid phosphate pollution, leading to wormlike phases [112]. Additionally, using Triethanolamine as hydrolysis retarding agent and CTAB as surfactant template, Cabrera et al. synthesized phosphorus-free wormlike, mesoporous TiO$_2$ [113].

**Figure 2.2.18** TEM photographs of (a) two dimensional hexagonal mesoporous titania along (110) zone axe, (b) dark-field TEM image of 2-d hexagonal mesoporous titania, (c) cubic mesoporous titania, and (d) N$_2$ sorption measurements of mesoporous titania [119].

Hydrogen peroxide was used as a hydrolysis-condensation inhibitor in basic media, leading to mesoporous TiO$_2$ [114]. In acid media, protons have been used to retard rapid condensation and generate titanium mesostructured oxosulfates [115] or mesoporous oxophosphates [116]. The use of non-aqueous solvents combined with complex agents has also been explored [117]. Using the tri-block copolymer as
templates, such as PEO20PPO70PEO20, Yang et al. [118, 119] synthesized many MTMO, including hexagonal mesoporous titania (see Figure 2.2.18a). The mesopore walls of mesoporous titania consists titania nano-crystals (~3nm (Figure 2.2.18b). Surface area up to 200m²/g can be obtained on cubic mesoporous titania (see Figure 2.2.18c, d) using EO75BO45 as template [119].

However, the mesoporous structure will collapse after removing the template by calcination. One of most important reasons is phase transformation [120]. In order to improve thermal stability, the mesoporous titania materials were treated by NH₃, which can inhibit the transformation from amorphous titania to anatase [121,122]. Cassier et al.[121] found that, during thermal treatment, the ammonia adsorbed in the pore channels promotes the transformation of some amorphous titania particles into thermodynamically stable and very small rutile crystallites before removal of templates by calcination (see Figure 2.2.19 left). The preformed rutile nano-crystallites limited the particle growth of the formed anatase phases [121]. High surface area and titania mesostructures constructed with walls consisting of rutile and anatase phases can be obtained after calcination. The mesostructures of synthesized mesoporous titania are stable upon calcination at 500 or even higher (see Figure 2.2.19 right).
Recently, there have been a few successes made in the syntheses of thermally stable titania films with crystalline walls based on the strategy of so-called evaporation induced self-assembly (EISA) [123–127]. The EISA method initiated by Brinker and co-workers for mesoporous silica film is also effective for the preparation of highly organised mesoporous TiO2 thin films [128]. In the EISA process, the evaporation of solvent, typically, ethanol, enriches the surfactant and inorganic species to form mesophases at the substrate-liquid, and liquid-air interfaces, resulting in well-defined mesostructured hybrids. Subsequent thermal treatment of the hybrids can produce ordered mesoporous frameworks.

The thermally stable titania films with nanocrystalline particles embedded in the amorphous matrix are all cubic mesostructures. However, attempts to obtain hexagonal mesostructure titania with highly crystalline framework and high thermal stability have been unsuccessful. In order to inhibit the growth of nanoparticles, stabilizing agents should be introduced before thermal treatment. In Sibu’s [129] report, La2O3 was used as a dopant to stabilise nano-anatase particles. Li et al. [130] prepared La3+ doped TiO2 photocatalyst by doping lanthanum ion into TiO2 structure in the sol–gel process. It is promising to stabilise the mesoporous titania with crystallized walls and to improve its photocatalytic activity by doping with La3+, which has so far proven to be successful [131].

2.2.3.3.2 Mesoporous nickel oxide and other mesoporous metal oxides

Nickel oxide is a material extensively used in catalysis, battery cathodes, gas sensors, electrochromic films, and magnetic materials. However, as far as mesoporous NiO is concerned, reports of its successful preparation are scarce. According to Nelson et al. [132], metallic nickel was electrodeposited from aqueous nickel (II) acetate dissolved in the lyotropic liquid crystalline phases of Brij 56 and Brij 78 surfactant templates to form metal films with hexagonal arrays of nanometre-sized channels. However, the templates were extracted by using 2-propanol extraction instead of burning off the organic templates by calcination. As reported by Banerjee et al. [133], as-synthesized
mesoporous NiO with template removed by extraction at room temperature are highly ordered as shown in Figure 2.2.20. However, after calcination at 500 °C for 2h, BET surface area dropped sharply from 278m²/g to 72m²/g, indicating the collapse of mesostructures. Similarly, high surface area can only be maintained upon calcination at low temperatures, for example at 350 °C [134].

![TEM photographs of as-synthesized mesoporous NiO (top) and textural parameters for mesoporous NiO (bottom) [133].](image)

### Table 2.2.21

<table>
<thead>
<tr>
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<th>pore volume (mL g⁻¹)</th>
<th>pore diameter (nm)</th>
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<td>0.457</td>
<td>3.68</td>
</tr>
<tr>
<td>400 °C calcined (4 h)</td>
<td>161.99</td>
<td>0.454</td>
<td>7.14</td>
</tr>
<tr>
<td>500 °C calcined (2 h)</td>
<td>72.61</td>
<td>0.156</td>
<td>6.84</td>
</tr>
<tr>
<td>air-dried unleached (110 °C)</td>
<td>213.53</td>
<td>0.28</td>
<td>3.72</td>
</tr>
</tbody>
</table>

**Figure 2.2.20** TEM photographs of as-synthesized mesoporous NiO (top) and textural parameters for mesoporous NiO (bottom) [133].

Besides mesoporous titania and nickel oxide, many other mesoporous metal oxides have also been synthesized, such as, Al₂O₃ [135-146], ZrO₂ [147-153], SnO₂ [154-157], Nb₂O₅ [158-166], Ga₂O₃ [167].

Therefore, it is clear that the synthesis of mesoporous titania with well ordered mesostructures is not easy, because the mesostructures are unstable upon removal of template by calcination at high temperatures. Many modifications to the synthesis
procedure were used to increase the stability of mesostructures, such as using the EISA method or adding different dopants like P or La2O3. Attempts to synthesise mesoporous NiO have not been successful. Functionalizing mesoporous silica could be, therefore, an easy and cheap alternative to MTMO materials.

2.3 Applications of functionalized mesoporous silica

As discussed above in section 2.2, the self-assembly of surfactant aggregates and mineral species can be tailored to provide mesoporous materials with high surface areas, extremely narrow pore size distribution, and perfectly adjustable pore size. Thus, mesoporous silica can find various applications to catalysis, adsorbents, molecular sieve and so on. For simplification, applications of mesoporous silica were divided in this section into five categories according to their typical roles such as: container, reactor, separator, template and support.

As to the application of mesoporous silica as support for catalysis, two kinds of catalyst systems are the focus of this project, one is nickel-containing mesoporous silica and the other is titania-containing mesoporous silica. Before reviewing the applications of nickel and titania-containing mesoporous silica to catalysis, the other four applications of mesoporous silica will be reviewed first.

**Container for drug delivery**

Lin et al [168] reported an MCM-41 type mesoporous silica nanosphere-based (MSN) controlled-release delivery system, which was synthesized using surface-derivatized cadmium sulfide (CdS) nanocrystals as chemically removable caps to encapsulate several pharmaceutical drug molecules and neurotransmitters inside the organically functionalized MSN mesoporous framework. This delivery system is schematically represented in Figure 2.3.1. It can be seen from this figure that the controlled-release mechanism of the system is based on chemical reduction of the disulfide linkage between the CdS caps and the MSN hosts.
Tanaka et al. have cleverly taken advantage of the post-synthetic grafting deficiency that leads to grafting near the pore opening to employ MCM-41 as a vehicle for drug delivery. They placed "hinged double doors" over the pore entrance that regulated the uptake and release of the host molecule cholestane by the mesopore [169]. Figure 2.3.2 shows the schematic of "hinged double doors" in the open and closed form. As shown in this figure, the photodimerizable coumarin [170] was tethered near the pore openings through a trialkoxysilyl terminated spacer. By using short grafting times and by performing the graft on uncalcined (surfactant filled) pores, considerable control in...
placing the coumarin molecule at the pore entrance was possible.

![Schematic of 'hinged double doors' in the open and closed form](image)

**Figure 2.3.2** Schematic of 'hinged double doors' in the open and closed form [169].

The photodimerization of coumarin is photo-reversible with the tethered dimer long enough to span the diameter of the MCM-41 pore (3 nm). Cholestane was chosen for its size; it is small enough to fit within the pore but too large to bypass the dimer. The containment and release of cholestane was determined by mass spectroscopic and thermogravimetric analyses. When open, the guest was almost completely removed upon washing. [169].

**Reactors**

The feasibility of forming polymer networks within the internal pore structure of porous materials was recently demonstrated. This was achieved through adsorption and subsequent polymerization of monomers in the mesoporous silica. Thus, Llewellyn et al. [171] adsorbed styrene, vinyl acetate, and methyl methacrylate (MMA) into MCM hosts with different pore sizes and studied the effect of confinement on polymer growth. An increase in the chain length of PMMA with decreasing pore size of MCM-41 was associated with inhibited termination processes in the channels.
Moller et al. [172] examined the polymerization of MMA in the mesoporous hosts MCM-41 and MCM-48 as well as in the microporous channels of zeolites NaY/X and ZSM-5. The monomers were introduced into the dehydrated and evacuated hosts from the vapour phase to avoid the formation of polymer layers on the external surface. Polymerization proceeded via radical initiation with high yield and resulted in nanocomposites with high polymer content. It is not surprising that the polymer dynamics change dramatically in the confinement of the host; on encapsulation, the glass transitions normally found in bulk polymers are suppressed. This result was observed in both the microporous as well as the mesoporous hosts.

In a related study, the adsorption of MMA in MCM-41 was also performed by Aida et al [173]. These authors observed that PMMA grown in the mesoporous channels of MCM-41 can exceed the bulk molecular weight by an order of magnitude; the chain length was controlled by the stoichiometry between the monomer and initiator. A novel twist to the use of mesoporous hosts was introduced by Mallouk, Ozin, and co-workers [174]. These authors formed a polymer mould of the channel structure of MCM-41, followed by dissolution of the host in HF. Phenol-containing MCM-41 was treated with formaldehyde vapour and HCl gas at elevated temperatures to form a cross-linked phenolic resin. After extraction from the host, polymer mesofibers that can visualize the length of the mesoporous channels were recovered [174].

**Separator**

The advantages of ordered silicate mesoporous materials for separation applications include a regular array of uniform pores, controllable pore size, and the ability to functionalize the surface for particular separations. Furthermore, MCM-41 has a rigid structure and so avoids the swelling problems encountered with some other adsorbents. Potential separation applications for MCM-41 include protein separation [175, 176] and mercury removal from waste streams [177, 178].
For example, the direct introduction of functionality into MCM-41 through the reaction with tris(methoxy)mercaptopropylsilane was achieved by two independent groups. In a large-pore Si-MCM-41 with 55 Å pore size, the concentration of thiol groups was varied and reached up to 76% of the full surface coverage (see Figure 2.3.3) [178]. The SH-moieties were subsequently used in both studies for removing mercury from waste streams. The highly efficient materials were also stable after regeneration by washing with concentrated HCl.

MCM-41 silicas have also then been proposed as possible stationary phases for size-exclusion chromatography [179], normal-phase HPLC [180, 181], capillary-gas chromatography [182], and chiral HPLC [183, 184].

**Template**

In section 2.2.3.3, the method of nanocasting was introduced. In this method, mesoporous silica is used as template for the synthesis non-silicon mesoporous
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materials. Upon the removal of mesoporous silica frameworks, open mesostructures can be obtained. Because a 3-D structure is necessary in the mould to maintain a stable replica, only experiments with MCM-48, MSU-1, and SBA-15 were successful. SBA-15 in principle has a unidimensional channel system. However, micropores seem to connect the linear hexagonally packed mesopores, thus providing the cross-linking necessary for obtaining a stable replica. MCM-41, on the other hand, proved to be less suitable for the production of porous carbons or metals.

![TEM image of ordered mesoporous SBA-15](image)

**Figure 2.3.4** (a, b) TEM image of an ordered mesoporous SBA-15, (c,d) mesoporous carbon obtained from “nanocasting” in a SBA-15 mould [193].

The preparation of ordered mesoporous carbons using ordered mesoporous materials as the templates has been reported [185-188]. Vix-Guterl et al.[189] first described the use of pure silica MCM-48 as the template to fabricate ordered mesoporous carbon. Subsequently, Xia and co-workers [190-192] reported the preparation and
characterization of ordered mesoporous carbon materials of various morphologies and structural types using SBA-15 silica template. To create graphitic pore walls, the authors employed the chemical vapour deposition (CVD) method with styrene and acetonitrile as the carbon precursors. However, the morphology of the replicated carbon particles was observed to be different from that of the SBA-15 template when CVD temperature was higher than 900 °C [190-192]. Figure 2.3.4 show the TEM photographs of synthesized mesoporous carbon. It can be seen that carbon mesostructures mimicking the mesostructures of SBA-15 can be obtained by CVD of benzene in the pores of mesoporous SBA-15 [193].

![Figure 2.3.4 TEM micrographs](image)

**Figure 2.3.4** TEM micrographs (left) of nanowires within the framework of SBA-15: (a) Au/SBA-15; (b) Ag/SBA-15; (c) Pt/SBA-15. The right is the TEM micrographs of the unsupported Pt nanowires obtained by removal of silica framework with aqueous HF solution [194].

Additionally, through direct impregnation of the mesoporous materials with precursor molecules or ions, followed by thermal or chemical reduction, noble metallic nanowires (such as platinum, palladium, gold, and silver) have been synthesized through this protocol [194-205]. Figure 2.3.5 shows the TEM micrographs of Ni, Ag, Pt-nanowires within the framework of SBA-15. It can be seen that pure Pt nanowires were obtained by removal of silica framework [194].

![Figure 2.3.5 TEM micrographs](image)
An alternative to the impregnation method, electrochemical deposition has also been explored to fabricate metal nanowires inside the channels of block copolymer and anodized alumina templates. Notably, metallic cobalt nanowires with diameters of 14 nm have been prepared by electrochemical deposition of cobalt inside channels formed by the self-assembly of block copolymers [206]. These dense magnetic arrays show enhanced coercivity, which points toward a route of ultra high-density magnetic storage media. Martin and coworkers [207] have pioneered the use of electroless deposition of metallic tubes inside channels of anodic alumina disks for novel separation applications. Zhang et al. [208] developed a new method to grow nickel and copper nanowires in functionalized powder SBA-15 through electroless deposition. The syntheses of nickel and copper nanowires inside the channels of SBA-15 with uniform dimension were achieved using palladium as catalysts. Additionally, Lu and
coworkers [209] prepared noble metal nanowire thin films by electrodeposition into porous silica thin-film templates. Macroscopically hierarchical thin films consisting of ordered arrays of noble metal nanowires were obtained.

Zhang et al. [210] also presented a new methodology of preparing one dimensional nickel nanowires using 2D hexagonal mesoporous silica films with p6mm symmetry as the template to generate ultra high density arrays of metallic nanowires inside ordered porous inorganic materials through a Pd-catalyzed electroless deposition process. Figure 2.3.6 shows the TEMs and SEMs of nickel-filled mesoporous silica film. It can be seen that the thickness of the nickel-filled film is uniform with a value of ~ 400 nm, as indicated by the SEM image shown in Figure 2.3.6a. Figure 2.5.6b shows an image of the as-synthesized mesoporous films after calcination, illustrating two-dimensional channels that are parallel to the substrate surface. After nickel deposition, the channels within the films were filled with foreign wire-like nanostructures, as illustrated by the bright field image in Figure 2.3.6c. It is clear from Figure 2.3.6c that nickel nanowires with an average diameter of ~ 8 nm are highly aligned and uniformly distributed across the film. The dark field image is shown in Figure 2.3.6d. As seen in Figure 2.3.6d, it is obvious that part of the image shows high bright contrast, indicating the presence of heavy elements inside the silica channels [210].

So far, the application of mesoporous silicas serving as container, separator, reactor, and template has been introduced. Now, the applications as supports for catalysis use, which, in fact, has been excellently reviewed [211, 212] will be discussed here. Because this project is dealing with the nickel, titania-functionalized mesoporous silica, only applications of nickel or titania-functionalized mesoporous silica will be reviewed.

2.3.1 Catalysis on nickel-containing mesoporous silica

For the nickel-containing mesoporous silica synthesized via a direct synthesis method,
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Hartmann et al. [58] synthesized nickel-containing MCM-41 and explored their catalytic application for ethylene dimerization and butene isomerization. They found that such materials were active in the selected reactions and moreover the ethylene dimerization activity and product distribution were different in different nickel-containing mesoporous silica. The activity for ethylene dimerization decreases in the order Ni/MCM-41 (DS method) > Ni-ALMCM-41 (ion-exchange) > Ni-MCM-41 (ion-exchange), which reflects the concentration of the catalytically active nickel (I) species (according to results of electron spin resonance).

Additionally, Parvulescu1 et al. [59], also synthesized nickel containing (3.6wt.% mesoporous silica. The catalytic activity and selectivity of these catalysts in liquid phase oxidation of 1-hexene, styrene and benzene with hydrogen peroxide were studied. Meanwhile, Ni-MCM-41 showed highest activity for liquid oxidation of 1-hexane compared with Co and Fe-containing MCM-41.

Additionally, MCM-41-supported nickel (3wt% nickel) catalysts were synthesized and their catalytic activity in hydrogenation of benzene was examined [96]. NiMo supported on MCM-41 was proven to be able to afford superior hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrocracking activities to amorphous silica-alumina and USY zeolite-supported Ni/Mo. Such superior performances were attributed to the uniform mesopores, high surface area, mild acidity and stability of MCM-41 [97]. (P)NiW and (P)NiMo-containing Ti-HMS with nickel oxide content of 3.17 and 3.44 wt.%, show higher activity in hydrogenation of naphthalene than the conventional alumina-supported catalysts [98]. KIT-1 supported NiO catalysts exhibit higher catalytic activities for thiophene hydrodesulfurization than similarly prepared MCM-41 and NaY zeolites supported catalysts. They attributed this to the three-dimensional disordered network of short channels in KIT-1, which reduces the risk of blockage in the catalysts and facilitates the transport of reactant and product molecules [99]. Rodríguez-Castellón et al. [100] reported that nickel (14.9 and 28.7 wt.% Ni) supported on a Zr-doped mesoporous silica (Si/Zr molar ratio of 5) was very
active in the hydrogenation of tetralin at 350 °C. The products molecules were also found as shown in Figure 2.3.7.

![Scheme of hydrogenation of tetralin](image)

Figure 2.3.7 Scheme of hydrogenation of tetralin [100].

Finely dispersed nickel particles supported on SBA-15 were evaluated to be active for the hydrodechlorination (HDC) of 1,1,2-trichloroethane (TCEa) as a model reaction [106].

### 2.3.2 Catalysis on titania-containing mesoporous silica

Firstly, the catalytic applications (mainly for epoxidation reactions) of Ti-containing mesoporous silica synthesized by DS method will be introduced.

Ti-MCM-41 was first studied for selectively epoxidizing olefins to epoxides using H₂O₂ as the oxidizing agent (Table 2.3.1) [50]. The advantages of Ti-MCM-41 as epoxidation catalyst is in its ability to oxidize large molecules which cannot diffuse in the pores of microporous materials, as well as to use organic hydroperoxides as oxidants. For instance Ti-MCM-41 was found to be much more active than Ti-β-zeolite to oxidize R-terpineol and norbornene at 70 °C using tert-butyl hydroperoxide as oxidant (Table 2.3.2) [50].
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Table 2.3.1 Catalytic oxidation of Hex-1-ene with H₂O₂ on Ti-MCM-41 [50].

<table>
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<th>selectivity (% molar)</th>
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<td>5.00</td>
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Table 2.3.2 Oxidation of α-Terpineol and Norbornene on Ti-containing materials [50].

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<th>epoxides</th>
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<tr>
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</tr>
<tr>
<td>Ti-Beta</td>
<td>3</td>
<td>4.1</td>
<td>2.5</td>
<td>5</td>
<td>4.7</td>
<td>5.6</td>
<td>6.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>7.6</td>
<td>5.8</td>
<td>11</td>
<td>11.2</td>
<td>7.1</td>
<td>12.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Ti-HMS showed a very high catalytic activity for the hydroxylation of benzene to phenol using acetone as the solvent. However, it was shown later [70] that the phenol yields were overestimated, due to the fact that the competitive oxidation of the acetone was not taken into consideration and the products formed were not separated chromatographically from phenol. Other papers have been published on this subject [54, 213, 214]. Recently it has been proposed that Ti-HMS prepared with a neutral surfactant (S*I*) exhibits greater catalytic activity for the liquid-phase peroxide oxidations of methyl methacrylate, styrene, and 2, 6-di-tert-butylphenol than Ti-MCM-41 [215].

Amines can also be oxidized on Ti-MCM-41 and Ti-HMS mesoporous materials [216, 217]. The products formed are of interest in several fields including chemical and pharmaceutical industries [218, 219]. While Ti-MCM-41 has little activity to convert primary aliphatic amines into the corresponding hydroxylamine, the mesoporous Ti-HMS is active for the oxidation of arylamines in the liquid phase. The success achieved from using the mesoporous material is attributed to the larger pores and the possibility of using organic peroxides as oxidants. On a similar basis, Ti-MCM-41 is able to oxidize bulky sulfides to the corresponding sulfoxides and sulfones, better than the Ti-β-zeolite [220].
The catalytic results for the epoxidation of styrene on Ti-SBA-15 with different contents of titanium are presented in Table 2.3.3. All of the samples show considerable activity, and the styrene conversion and epoxidation selectivity depend strongly on the Ti content in the Ti-SBA-15 materials. For example, sample 4 has a styrene conversion of 38.2% and an epoxidation selectivity of 49.7% [57].

Table 2.3.3 Catalytic results for the epoxidation of styrene on Ti-SBA-15 [57].

<table>
<thead>
<tr>
<th>Sample</th>
<th>TiSil (initial gel) (mol %)</th>
<th>TiSil (final product) (mol %)</th>
<th>Surface area (m²/g)</th>
<th>Pore diameter (nm)</th>
<th>Pore volume (mL/g)</th>
<th>Conversion of styrene (mol %)</th>
<th>Selectivity (mol %)</th>
<th>Benzaldehyde</th>
<th>Epoxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>0.10</td>
<td>964.2</td>
<td>9.58</td>
<td>1.177</td>
<td>9.9</td>
<td>55.2</td>
<td>41.8</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>0.21</td>
<td>1044.0</td>
<td>9.74</td>
<td>1.193</td>
<td>10.3</td>
<td>51.2</td>
<td>48.8</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.5</td>
<td>0.43</td>
<td>1044.5</td>
<td>9.75</td>
<td>1.157</td>
<td>38.2</td>
<td>50.3</td>
<td>49.7</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2.0</td>
<td>0.66</td>
<td>1009.5</td>
<td>9.64</td>
<td>1.057</td>
<td>37.2</td>
<td>52.7</td>
<td>47.3</td>
<td></td>
</tr>
</tbody>
</table>

* Conversion (mol %) = (converted styrene/TiO₂) x 100

Titania-containing mesoporous silica synthesized via the post-synthesis method often shows activity for photo-degradation of organic pollutants. Zheng et al. [89] reported the synthesis of Ti-containing MCM-41 for degradation of phenol in water. They found that Ti-containing MCM-41 showed a relatively high photocatalytic activity compared to crystalline TiO₂ such as anatase or a TiO₂-SiO₂ composite oxide.

Well dispersed titania (TiO₂)n (n~30-70) clusters attached to the silica walls of MCM-41 were found to be active for the photobleaching of rhodamine-6G and oxidation of α-terpineol [90]. Grieken et al. [92] synthesized SBA-15-supported titania particles and concluded that titania particles with size of about 7nm supported on SBA-15 was more photoactive. Belhekar et al. [93] reported titania-containing HMS and studied the photo-degradation activities for removal of basic dye namely methylene blue and organic pollutants like phenol and toluene on titania-containing mesoporous silica.
2.4 Current problems and the solutions

It is still not easy to synthesize mesoporous titania with well ordered mesostructures that are not stable upon removal of template by calcination at high temperatures. For mesoporous titania, many modifications to the synthesis procedure are needed to increase the stability of mesostructures, such as using the EISA method or adding different dopants like P, La$_2$O$_3$. As for the synthesis of mesoporous NiO, attempts up to now have not succeeded. Functionalizing mesoporous silica is, therefore, an easy and cheap alternative to MTMO materials.

On the other hand, for nickel-containing mesoporous silica, it is difficult to load high amounts of nickel without damaging the mesostructures by using the DS method [58-59]. So far, no report has been published on the synthesis of MCM-41-type silica with higher nickel content than 3.6wt.% using the DS method [59]. For the titania-containing mesoporous silica synthesized via the post-synthesis method, loading high amounts of titania at a time into the mesochannels often leads to the blockage of mesopores due to the formation of big titania particles [92, 93].

In the DS method for the synthesis of Ni-containing mesoporous silica, the rapid precipitation of nickel ions in basic conditions does not allow full interaction with the template molecules, which results in the low loading into the mesophases and formation of extra-framework NiO after calcination. In order to heighten the nickel content in the DS method, a possible solution is to restrict the formation of bulk NiO and take advantage of the interaction between silica species and template molecules. In order to synthesize mesoporous silica with high amounts of titania without blockage of mesopores using the post-synthesis method, increasing the dispersion of titania species as high as possible might be a solution.

Therefore, in this project, a modified the DS method and a multistep impregnation route will be developed to prepare high nickel-containing mesoporous silica and high titania-containing mesoporous silica, respectively.
Chapter 2 Reviews on mesoporous materials: synthesis and applications

References


55
[51] K. M. Reddy, I. L. Moudrakovski, A. Sayari, Recent Research Reports, 10th
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Chapter 3 Characterization of mesoporous materials

3.1 Introduction

Characterization of mesoporous materials constitutes an important aspect of this project, including the examination of mesostructures, functional species loaded in mesoporous silica and assessment of catalytic performance. Many principles of characterization and methods for data analysis (including many calculation models) need to be introduced. Therefore, an independent chapter is allocated for characterization of mesoporous materials.

Many techniques have been employed in this project to characterise the mesostructures of synthesized mesoporous materials, such as X-ray diffraction (XRD), small-angle XRD, transmission electron microscopy (TEM), and scanning tunnelling microscopy (STM), nitrogen sorption measurements. According to the techniques used in this project, most often used method of low-angle XRD and nitrogen sorption characterisation techniques will be introduced.

As to the characterisation of Ni or Ti species incorporated into the mesoporous silica, techniques like Fourier transformation infrared (FTIR) Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), Ultra-violet visible absorption spectroscopy and diffuse reflectance spectroscopy (UV-vis-DRS) will be introduced as well.

3.2 X-ray diffraction

It is well known that powder XRD is extensively used to obtain information from crystalline materials, but is quite useless for the characterisation of amorphous materials. Here, some useful information needed for a better understanding of application of low-XRD to characterisation of mesostructures is discussed.

3.2.1 Elemental crystallography

Crystals consist of a regular three-dimensional arrangement of atoms, ions, or molecules. This implies that there is a basic repeating unit that is the unit cell whose
size and shape can be defined in terms of six parameters: a, b, c, α, β, and γ, as shown in Figure 3.2.1. Mathematical analysis shows that there are seven possible shapes for a unit cell; they are given in Table 3.2.1.

**Figure 3.2.1 Unit cell parameters.**

**Table 3.2.1 Seven crystal systems**

<table>
<thead>
<tr>
<th>System</th>
<th>Parameters</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>a=b=c</td>
<td>α=β=γ=90°</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>a=b≠c</td>
<td>α=β=γ=90°</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>a=b≠c</td>
<td>α=β=90° γ=120°</td>
</tr>
<tr>
<td>Rhombohedral</td>
<td>a=b=c</td>
<td>α=β=γ≠90°</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>a≠b≠c</td>
<td>α=β=γ=90°</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>a≠b≠c</td>
<td>α=β=90° γ≠</td>
</tr>
<tr>
<td>Triclinic</td>
<td>a≠b≠c</td>
<td>α≠β≠γ≠90°</td>
</tr>
</tbody>
</table>

If a unit cell has the same type of atom at the corners of the unit cell but neither in the middles of the faces nor right in the centre of the cell, it is called primitive, and give the symbol P. They are also three types of non-primitive cell: body centred, Symbol I; face centred, symbol F; end centred, symbol C. Nevertheless, there are totally only 14 categories (Figure 3.2.2):
3.2.2 Families planes

Figure 3.2.3 shows part of a primitive hexagonal structure \((a=b\neq c, \alpha=\beta=90^\circ, \gamma=120^\circ)\) with family of planes indicated by shading. Such planes contain all the atoms in the lattice. The repeating distances between the adjacent planes are called d-spacing. Families of planes are identified by a set of Miller Indices, which are given the symbols \(hkl\), and can take only integer values. Meanwhile, the values of \(h, k, l\) are the numbers of segments which they are divided into on edges \(a, b, c\), respectively. For example, \(a\) is divided into two segments, then \(h = 2\), no division on \(b\) and \(c\) means \(k, l = 0\), thus the Miller Indices of the family of planes in Figure 3.2.3, the top one is \([100]\)
and the bottom is [200]. The d-spacing and the unit cell can be calculated from the Bragg Equation as described below. It is easy to know \( d_1 = 2d_2 \).

![Diagram of hexagonal P system](image)

**Figure 3.2.3** Families planes of hexagonal P system.

### 3.2.3 Applications of X-ray diffraction to mesoporous materials

XRD has been widely used as a powerful tool for knowing the mesostructural ordering of the mesoporous material. The information from the XRD can be used to estimate the geometry of the array, whether it is hexagonal or cubic. Although the frameworks of mesoporous silica are usually amorphous to X-rays, the contrast between the silica walls and channel space can generate X-ray scattering. Therefore, the prerequisite to produce the X-ray scattering is fulfilled for long-range ordered mesoporous materials. Thus, low-angle XRD can be used to examine the long-range mesostructural ordering of synthesized mesoporous materials.

Table 3.2.2 reveals common XRD patterns for hexagonal mesoporous structure. The MCM-41 lattice can be indexed as a hexagonal unit cell with \( a = b \) and \( c = \infty \). Because the parameters \( a \) and \( b \) are in the order of nanometres instead of tenths of nanometres
as usually encountered in crystals, X-ray diffraction occurs only in low-angle regions as shown in XRD pattern included in Table 3.2.2.

<table>
<thead>
<tr>
<th>Mesophase model</th>
<th>XRD pattern</th>
<th>TEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>hexagonal</td>
<td><img src="image" alt="XRD pattern" /></td>
<td><img src="image" alt="TEM image" /></td>
</tr>
</tbody>
</table>

**Table 3.2.2** Hexagonal structure and corresponding XRD pattern [1].

**Figure 3.2.4** The Bragg condition.
### 3.2.4 Bragg equation

The 'birth' of X-ray crystallography occurred in June 1912 with the publication of the first X-ray diffraction patterns of copper sulphate and zincblende by von Laue and assistants Friedrich and Knipping. But, how can the crystal structures be determined from such X-ray diffraction patterns? W.L. Bragg devised a simple approach based on the reflection of X-rays by planes of atoms.

Figure 3.2.4 shows the schematic representation of Bragg condition. It can be seen from this figure that for the path difference \((GY+YH) = 2dsin(\theta)\). The two reflected rays XD and YE will interfere when the path difference is equal to the wavelength \((\lambda)\) or a multiple of it (see Figure 3.2.4(II)):

\[
2d \sin(\theta) = n\lambda
\]

This is Bragg equation. Diffraction would occur if the Bragg condition was met for particular family of planes.

### 3.2.5 Calculations of d-spacing, unit cell and pore wall thickness

<table>
<thead>
<tr>
<th>hkl</th>
<th>2-theta</th>
<th>d-spacing(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>2.36</td>
<td>37.4</td>
</tr>
<tr>
<td>110</td>
<td>4.10</td>
<td>21.5</td>
</tr>
<tr>
<td>200</td>
<td>4.72</td>
<td>18.7</td>
</tr>
<tr>
<td>210</td>
<td>6.26</td>
<td>14.1</td>
</tr>
</tbody>
</table>

**Figure 3.2.5** Low-angle XRD pattern of a mesoporous material.
Figure 3.2.6 Representation of hexagonal mesopore structures, OA is unit cell, a, OB is D/2 (D is known mesopore size, such as 3.0nm), OC is d_{100}. Dark regions denote the frameworks inside which it is the mesopores.

Figure 3.2.5 shows an example of XRD pattern for a mesoporous material. Here, an example is used to illustrate the calculation of d-spacings, unit cell and pore wall thickness using Bragg equation according, assumed that the mesostructures are in hexagonal geometry and pore size is known, for example 3.0nm. Figure 3.2.6 shows the illustration of hexagonal mesopore structures. The d_{100} can be calculated using Bragg equation, therefore,

\[ d_{100} = \frac{\lambda_{X\text{-ray}}}{2\sin(\theta)} \]

Here, \( \lambda_{X\text{-ray}} \) is constant and equal to 0.1542 nm and \( \theta \) corresponds to the angle at which (100) reflection locates in the low-angle XRD pattern (Figure 3.2.5, in which \( 2\theta = 2.36^\circ \)). This yields,

\[ d_{100} = \frac{0.1542}{2\sin\left(\frac{1.18 \times 2\pi}{360}\right)} = 3.74\,nm = 37.4\,\text{Ångstroms} \]

Similarly, it is easy to calculate \( d_{110}, d_{200}, d_{210} \) and so on.

According to Figure 3.2.6 the unit cell \( a \) and pore wall thickness \( t \) can be calculated, apparently,
\[ a = \frac{2}{\sqrt{3}} d_{100} = 4.32 \text{nm} \]

\[ T = a - D = 4.32 - 3.0 = 1.32 \text{nm} \]

3.3 Nitrogen sorption

N\textsubscript{2} adsorption measurement can offer much important information on the surface area and porous structures that cannot be obtained through other approaches. Nomenclatures, different models and the equations used in N\textsubscript{2} sorption measurements need to be interpreted.

3.3.1 Classification of the pore sizes

The pore systems of solids are of much different kind. The individual pores may vary greatly both in size and in shape within a given solid, and from one solid to another. A convenient way to classify them according to their average width has originally been proposed by Bubinin [2, 3] and now officially adopted by the IUPAC (Table 3.3.1). From this table, it can be seen that mesoporous materials can be simply understood as porous materials with pore width ranging from 2 nm to 50 nm.

<table>
<thead>
<tr>
<th>Pore types</th>
<th>Pore widths</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micropores</td>
<td>less than (\sim 20 \text{\AA}) (2 nm)*</td>
</tr>
<tr>
<td>Mesopores</td>
<td>between (\sim 20) and (\sim 500 \text{ \AA}) (2 and 50 nm)</td>
</tr>
<tr>
<td>Macropores</td>
<td>more than (\sim 500 \text{ \AA}) (50 nm)</td>
</tr>
</tbody>
</table>

*1 nm = 10 \(\text{\AA}\) = 10\(^{-9}\) m

3.3.2 Adsorption and desorption isotherms

When a solid such as charcoal is exposed in a closed space to a gas or vapour at some definite pressures, this solid will adsorb the gas, which results in the increase in the weight of the solid and decrease in the pressure of the gas. The pressure will later arrive to a constant value, which can be determined by calculating from the fall of the
pressure by application of the gas laws, if either the volumes of the vessel and of the solid are known or they can be determined directly from the increase in the weight of the solid.

In such experiment, the gas adsorbed by the solid (adsorbent) is termed adsorbate. The adsorption is brought about by the forces acting between the solid and the molecules of the gas, which always include 'dispersion' force, which are attractive, together with short-range repulsive forces. In addition, there will be electrostatic forces if either the solid or the gas is polar in nature.

![Diagram of adsorption isotherms](image)

**Figure 3.3.1** Five types of adsorption isotherms, I to VI, in the classification of BDDT [4a]. Oxygen on charcoal at 90K shows Type I isotherm [4b]; nitrogen on iron catalysts at 78K shows Type II [4c], bromine on silica gel at 352K shows Type III [4d], benzene on ferric oxide gel at 323K shows Type IV [4e], and water vapour on charcoal at 373K shows Type V [4f].

Isotherms for N₂ sorption are plots of the amount of N₂ adsorbed on adsorbent against the N₂ relative pressures. The majority of the isotherms can conveniently be grouped into five classes. Five types from I to V of the classification originally were proposed by Brunauer, Deming, Deming and Teller (hereafter BDDT) [4a], as shown in the Figure 3.3.1. The Type VI isotherm, although scarce, was also observed [5]. Type IV isotherm is the focus in this project, because all the mesoporous materials synthesized
can give Type IV isotherm. Deeper understanding of the type IV will provide a reasonable estimate of the specific surface area, pore volume and an appropriate assessment of the mesopore size distribution.

In order to provide an interpretation of these isotherms, Zsigmondy put forward his capillary condensation theory, which in one form or another has served as a basis for virtually all subsequent theoretical treatments of type IV isotherms [6]. Zsigmondy made use of the principle, which had been established some time earlier by Thomson (later, Lord Kelvin) on thermodynamic grounds, that the equilibrium vapour pressure, $p$, over a concave meniscus of liquid, must be less than the saturation vapour pressure, $p^\circ$, at the same temperature. This implies that the vapour will be able to condense to liquid in the pores of a solid, even when its relative pressure is less than unity [7].

![Figure 3.3.2 Type IV isotherm. In comparison, Type II isotherm follows the course ABCN (dashed line) [8].](image)

Figure 3.3.2 shows the Type IV isotherm that helps to illustrate the model proposed by Zsigmondy [8], which in broad terms is still accepted. This model assumes that along the initial part of the isotherms (ABC in Figure 3.3.2), adsorption is restricted to a thin layer on the walls, until at D (the inception of the hysteresis loop with adsorption branch DEG and desorption branch FJD) capillary condensation commences in the
finest pores. As the pressure is progressively increased, wider and wider pores are filled until at the saturation pressure the entire system is full of condensate. As the saturation pressure is approached, the amount of adsorbed may show little variation (along FGH) or alternatively there may be a final upward turn (GH').

There were many efforts devoted to link the adsorption data to the pore size. Thomson's original equation is not suitable for direct application to adsorption data. Kelvin's equation has been extensively used by later workers, that is

$$\ln \frac{p}{p^0} = \frac{-2\gamma V_L}{RT} \frac{1}{r_m}$$  \quad \text{eq. (3.3.1)}

Here, $p/p^0$ is the relative pressure of the vapour in equilibrium with a meniscus having radius of curvature $r_m$. $\gamma$ and $V_L$ are the surface tension and molar volume respectively. $R$ and $T$ have their usual meanings.

Following Zsigmondy, the earlier workers in this field assumed the pores to be cylindrical and the angle of contact to be zero, so that the meniscus was hemispherical. The mean radius of curvature $r_m$ thus became equal to the radius of the pore less the thickness of the adsorbed film on the walls. Therefore, using Kelvin equation, it is possible to calculate the minimum radius of pores in which capillary condensation can take place from the relative pressure at D (Figure 3.3.2), the lower limit of the hysteresis loop. Similarly, the applicable upper limit of the Kelvin's equation, $r_m \sim 25\text{nm}$, is a practical one, considering the experimental difficulty to measure very small lowerings of vapour pressure. Thus, the justification for defining mesopores by reference to the limits of 1~25 nm rests upon the fact that classical capillary equations, especially the Kelvin equation, are applicable in this range.

A number of the attempts have been made to demonstrate the connection between the mesoporosity and the Type IV isotherm by comparing the isotherm of a vapour on a nonporous powder before and after it has been formed into a compact. Many results
demonstrate that the presence of the mesopores brings about an increase in adsorption, and that capillary condensation hypothesis offers the most reasonable explanation.

![Figure 3.3.3 Four kinds of the hysteresis loops defined by IUPAC [8].](image)

Certain shapes of hysteresis loops are associated with specific pore structure. A classification of the hysteresis loops, as recommended in IUPAC manual, consists of four types as shown in Figure 3.3.3. Type H1 loops are often obtained with agglomerates or compacts of spheroidal particles of fairly uniform size and array. Some corpuscular systems tend to give H2 loops, but the distribution of the pore size and shape is not well defined. H3 and H4 can be obtained with adsorbents having slit-shaped pores or plate-like particles (in case of Type 3).

![Figure 3.3.4 A typical N$_2$ sorption isotherm for MCM-41-type mesoporous silica.](image)
An example to explain the adsorption of N\textsubscript{2} on mesoporous surface in different regions is given in Figure 3.3.4. It can be seen from this figure that, at very low relative pressure (p/p\textsubscript{0}) (region I), a very large amount of nitrogen (because of the high surface area and possibly presence of micropores) becomes physisorbed, which is normally associated with the monolayer adsorption of nitrogen on the surface and condensation in micropores. Upon monolayer adsorption, multilayer adsorption will take place at higher relative pressures (region II), followed by a sharp increase of adsorbed nitrogen, due to the nitrogen capillary condensation in mesopores (region III). The Kelvin equation describes the relation between mesopore size and relative pressure. The desorption and adsorption curves overlap significantly giving a very narrow hysteresis loop, which is characteristic for cylindrical pores. After complete filling of mesopores, multilayer adsorption of nitrogen on the outer silica surface happens (region IV). Such almost level curves show that the external surface area is pretty small. Region V can be attributed to the condensation of nitrogen within voids between the bulk particles. Much information can be derived from this isotherm, such as BET surface area, porosity (microporosity and mesoporosity), and pore size distributions.

3.3.3 Pore size distributions
How to calculate the mesopore size distributions is important. The commonly used method for analyzing mesopore size distributions is the Barrett–Joyner–Halenda (BJH) model [9]. Although this method was reported to underestimate pore sizes for diameter <6.5 nm [8, 10-14] to a certain extent, BJH model was still used in this project because it is useful for comparison purposes. The calculations were performed from the adsorption isotherm using the relations between the pore diameter and the relative pressure p/p\textsubscript{0}.

To calculate the pore size distributions, it is necessary to introduce the Kelvin function first on thermodynamic grounds and how it can be used to calculate the cylindrical pore size from adsorption data. The equilibrium vapour pressure, p, over a concave
meniscus of liquid, must be less than the saturation vapour pressure, \( p^0 \), at the same
temperature. This implies that a vapour will be able to condense to a liquid in the pores
of a solid, even when its relative pressure is less than unity. Equation 3.3.2 is the
conventional form of the Kelvin function, which is the related equilibrium vapour
pressure of a curved surface, such as that of a liquid in a capillary or pore, to the
equilibrium pressure of the same liquid on a plane surface.

\[
\ln \frac{p}{p^0} = -\frac{2\gamma V_L}{RT} \frac{1}{r_k} \cos(\theta) \quad \text{eq. (3.3.2)}
\]

Where \( p \) is the equilibrium vapour pressure of liquid in pores with radius \( r_k \), and \( p^0 \) is
the equilibrium pressure of the same liquid on a plane surface. The terms of \( V_L \) and \( \gamma \)
are the surface tension and molar volume of the liquid, respectively; \( \theta \) is the contact
angle with which the liquid meets the pore walls.

The Kelvin equation can be derived on thermodynamic grounds considering the
transfer of \( d_n \) moles of vapour in equilibrium with the bulk liquid at pressure \( p^0 \) into a
pore where the equilibrium pressure is \( p \). This process consists of three steps:
evaporation from the bulk liquid, expansion from \( p^0 \) to \( p \) and condensation into the
pores. The first and third step are equilibrium processes and therefore accompanied by
a zero free energy change, whereas the free energy change for the second step can be
described by

\[
dG = -RT \ln \frac{p}{p^0} d_n \quad \text{eq.(3.3.3)}
\]

When the adsorbate condenses in the pores, it does so on a previously adsorbed film
thereby decreasing the film-vapour interfacial area. The free energy change associated
with the filling of the pores is given by

\[
dG = -(\gamma \cos \theta) dS \quad \text{eq.(3.3.4)}
\]

Where \( \gamma \) is the surface tension of the adsorbed film, assumed to be identical with that of
the liquid, \( dS \) is the change in interfacial area and \( \theta \) is the wetting angle which is taken
to be zero (\( \cos(\theta)=1 \)) since the liquid is assumed to wet completely the adsorbed film.
Therefore, eq.(3.3.3) and (3.3.4) yield
The volume of liquid adsorbate which condenses in a pore of volume $V_p$ is given by

$$dV_p = V_L dn$$  

where $V_L$ stands for the molar volume of the liquid adsorbate. Therefore, eq. (3.3.5) and (3.3.6) yield

$$\frac{dV_p}{dS} = \frac{-\gamma V_p}{RT \ln p / p^0}$$  

The ratio of volume to area within a pore depends on the pore geometry. For instance, the volume to area ratios for cylinders, parallel plates and spheres are $r_k/2$, $r_k/2$, and $r_k/3$, respectively, where $r_k$ is the cylinder and sphere radii or the distance of separation between parallel plates. In many cases without specific knowledge of the pore geometry, the assumption of cylindrical pores is usually made, so eq. (3.3.7) becomes

$$\ln \frac{p}{p^0} = -\frac{2\gamma V_L}{RT} \frac{1}{r_k}$$  

Eq. (3.3.8) is the working equation for the pore size analysis by adsorption. For the nitrogen physical adsorption experiments, here, $p/p^0$ is the relative pressure of the vapour in equilibrium with a meniscus having a radius of curvature $r_k$; $\gamma$ (8.88 mN m$^{-1}$) and $V_L$ (36.48 ml mol$^{-1}$) are the surface tension and molar volume of liquid nitrogen, respectively; $R$ (8.314 J (mol K)$^{-1}$) and $T$ (77 K) have their usual meanings. So

$$r_k = \frac{4.15}{\log(p / p^0)} \text{ (Å)}$$  

Therefore, using eq. (3.3.9), the minimum pore radius of cylindrical pores in which capillary condensation can take place can be calculated. This term $r_k$, called Kelvin radius or critical radius, is often not the actual pore radius since some adsorption has already take place on the pore walls prior to condensation leaving a centre core or radius $r_k$. Alternatively, during desorption, an adsorbed films remains on the pore walls when evaporation of the centre core take place. If the depth of the adsorbed film when condensation (in the thesis, all pore distributions calculation are based on the adsorption data) occurs is $t (p/p^0)$, then
Chapter 3: Characterization of mesoporous materials

\[ r_p = r_k + t(p/p^0) \]  \hspace{1cm} \text{eq. (3.3.10)}

And \( r_p \) is the actual pore radius size used for the plots of pore distributions. According to Halsey equation [15], the adsorbed layer thickness \( t(p/p^0) \) can be written as

\[ t(p/p^0) = 3.54 \left( \frac{5}{2.303 \log(p^0/p)} \right)^{\frac{1}{3}} \]  \hspace{1cm} \text{eq. (3.3.11)}

So the relationships between the relative pressure and pores size can be made. To calculate the pore size distribution, the work sheet (see Table 3.3.2) and the corresponding explanation of each column are given. The adsorbed volumes are from the experimental results of one kind of mesoporous silica. The procedure used as shown in Table 3.3.2 is the numerical integration method of Pierce [16] as modified by Orr and Dalla Valle [17] regarding to the calculation of the depth of the adsorbed film. It is assumed that a multilayer of adsorbed film exists on the pore walls when evaporation or condensation occurs, which is the same depth as the adsorbed film on a nonporous surface.

**Table 3.3.2 working-table for the calculation of pore size distributions of mesoporous silica.**

<table>
<thead>
<tr>
<th>( p/p^0 ) (ml/g)</th>
<th>( V_{pm} ) (A)</th>
<th>( r_k ) (A)</th>
<th>( t ) (A)</th>
<th>( r_p ) (A)</th>
<th>( \bar{r}_k )</th>
<th>( \bar{r}_p )</th>
<th>( \Delta t ) (A)</th>
<th>( \Delta V_{pm} ) (ml/g)</th>
<th>( \Delta V_{liq} ) (ml/g)</th>
<th>( \Delta t \Sigma s ) (ml/g)</th>
<th>( V_p ) (ml/g)</th>
<th>( S )</th>
<th>( \Sigma s )</th>
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<td>645.631</td>
<td>670.296</td>
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<td>0.00341</td>
<td>1.02E-05</td>
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<td>4.63E-05</td>
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<td>506.451</td>
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<td>451.864</td>
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<td>331.542</td>
<td>351.271</td>
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<td>208.797</td>
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<td>1.812</td>
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<td>131.747</td>
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<td>90.054</td>
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</tbody>
</table>
The method shown in Table 3.3.2 uses the data from the adsorption isotherm and the data are evaluated downward from high to low relative pressures.

Column 1 and 2: $N_2$ relative pressure and amount of $N_2$ adsorbed volume on 1.0 gram of the adsorbent, obtained directly from the adsorption isotherm.

Column 3: Kelvin radius, as calculated using eq. (3.3.8).

Column 4: film depth, $t$, is calculated using eq. (3.3.11).

Column 5: addition of column 3 to 4, as shown in eq. (3.3.10).

Column 6 and 7: calculating the mean value in each decrement from successive entries.

Column 8: the change in film depth, $\Delta t$, is calculated as the difference between successive $t$ values.

Column 9: $\Delta V_{gas}$, is the difference between successive $V_{gas}$ values (as shown in column 2)

Column 10: $\Delta V_{liq}$ is the corresponding liquid $N_2$ volume to Column 9—multiply by 0.001547 for $N_2$ at STP.

Column 11: $\Delta t\Sigma s$ represents the volume change of the adsorbed film remaining on the pore walls from which the centre cores have been evaporated, assuming no pores are larger than 950Å ($p/p^0=0.99$). The first entry in column is zero because there is no film area from previously emptied pores. The error introduced by this assumption is negligible because the area produced by pores larger than 950Å will be small compared to their volume. Subsequent values in column 11 are calculated as the
product of $\Delta t$ for a decrement and $\sum S$ from the row above corresponding to the adsorbed film area exposed by evaporation of the centre cores during all the previous decrements.

Column 12: the actual pore volume, is determined by recalling that the volume of liquid (column 10) is composed of the volume evaporated out of the centre cores plus the volume desorbed from the film left on the pore walls, that is

$$V_p = \left( \frac{\bar{r}_p}{\bar{r}_k} \right)^2 \left[ \Delta V_{Liq} - \Delta t \Sigma S \times 10^{-4} \right] \text{cm}^3 \quad \text{eq. (3.3.12)}$$

because,

$$\Delta V_{Liq} = \pi \bar{r}_k^2 l + \Delta t \Sigma S \quad \text{eq. (3.3.13)}$$

and

$$V_p = \pi \bar{r}_p^2 l \quad \text{eq. (3.3.14)}$$

Where, $l$ is the pore length.

Column 13: $S$ is the surface area of pore walls calculated from the pore volume by

$$S = \frac{2V_p}{\bar{r}_p} \times 10^4 \text{ (m}^2) \quad \text{eq. (3.3.15)}$$

Column 14: the sum of column 13.

At last, the pore size distributions curve are plotted, $\Delta V_p/\Delta r_p$ (from the column 12 and 5, respectively) against $\bar{r}_p$, (shown in column 7), as shown in Figure 3.3.5. It is clear that the most probable distributed mesopore size is 7.2 nm in diameter.
3.3.4 \( \alpha_s \)-plots analysis

Gas adsorption is an important method for evaluating the specific surface area, pore volume, pore size, and pore size distributions and to study surface properties of these materials [18-19]. There are several methods, such as \( t \)-plots, \( \alpha_s \)-plots, \( \theta \)-plots [19], which are suitable primarily for evaluation of the specific surface area, including external surface area and mesoporous surface area, microporous surface area, pore volume. In this section, how to use the \( \alpha_s \)-plots analysis to qualitatively characterise microporosity will be introduced.

Recently, comparative analysis was also shown to provide a convenient way to study the surface properties of porous solids [19], which is based on the comparison of adsorption isotherms for porous solids under study with the adsorption isotherm for a proper macroporous reference solid [19, 20]. Usually, one chooses a macroporous reference adsorbent, which has surface properties (with respect to the adsorbate used) similar to those of the solid under study. This is because differences in the surface

Figure 3.3.5 Pore size distributions of mesoporous silica.
properties will cause nonlinearity of comparative-plot curves even if adsorption on the compared solid proceeds exclusively via multilayer formation.

In such a case, the analysis of the comparative plots is based on the following principles: (1) Adsorption on the macroporous reference solid proceeds via multilayer formation, whereas the course of adsorption on the compared solid depends upon sizes of pores. (2) Adsorption in macropores takes place in the same way as on the reference solid, that is, via multilayer formation. In the case of micropores, adsorption proceeds via micropore filling at lower relative pressures, and in the case of mesopores, there is a multilayer formation followed by capillary condensation.

In this project, the most samples are silica-like materials; therefore the focus is on how to evaluate surface properties, especially the pore volume of silicas. To facilitate the application of comparative analysis in the characterization of porous silicas, a nitrogen adsorption isotherm measured in a wide range of relative pressures (from about $10^{-6}$ to 0.97) for carefully selected macroporous silica, LiChrospher Si-1000, was reported by Jaroniec et al. [20]. LiChrospher Si-1000 was studied by Kurganov et al. [21] and was shown to be essentially amorphous and free from crystalline constituents. It was also demonstrated that nitrogen adsorption properties of various chromatographic silica gels are very close to one another [20-24] and highly similar to those of various ordered mesoporous silicas with amorphous pore walls [22, 35-27].

Table 3.3.3 shows the N$_2$ adsorption isotherm data for LiChrospher Si-1000 Silica collected by Jaroniec et al.[20]. As shown in Table 3.3.3, amounts of N$_2$ adsorbed were divided by the amount adsorbed at the relative pressure of 0.4, that is, 9.1248 cm$^3$ STP g$^{-1}$. Such adsorption data will be used to carry out porosity analysis of synthesized mesoporous samples [20]. Therefore, Figure 3.3.6 shows the $\alpha_s$ curve, in which $\alpha_s$ was plotted against the relative pressure. This curve will then be utilized for the $\alpha_s$/t-plots analysis by redrawing a curve of amount adsorbed ($y$-axis) plotted against $\alpha_s$ ($\alpha_s$-plots) or $t$ (t-plots) ($x$-axis) rather than against relative pressure, $p/p_0$. 

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Table 3.3.3 Standard Reduced Nitrogen Adsorption Isotherm Data for LiChrospher Si-1000 Silica [20]a.

<table>
<thead>
<tr>
<th>( p/p_0 )</th>
<th>( \alpha_0 )</th>
<th>( p/p_0 )</th>
<th>( \alpha_4 )</th>
<th>( p/p_0 )</th>
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<th>( \alpha_6 )</th>
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<td>0.550</td>
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<td>1.01 \times 10^{-3}</td>
<td>0.276</td>
<td>0.02300</td>
<td>0.510</td>
<td>0.5000</td>
<td>1.109</td>
<td>0.986</td>
<td>2.816</td>
</tr>
<tr>
<td>1.18 \times 10^{-3}</td>
<td>0.284</td>
<td>0.03000</td>
<td>0.528</td>
<td>0.5250</td>
<td>1.135</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a: the adsorbed amounts can be obtained by multiplying the \( \alpha_0 \) data by 9.12 cm³ STP g⁻¹. The statistical film thickness curve can be obtained by multiplying the \( \alpha_0 \) data by 0.722 nm. Data in parentheses were obtained using the nitrogen adsorption isotherm for LiChrospher Si-4000 silica.

Figure 3.3.6 \( \alpha_0 \) curve of LiChrospher Si-1000 silica.
To determine whether the pores present in the sample are micropores, mesopores, or macropores, one can simply plot the amount adsorbed on the porous solid under study as a function of the amount adsorbed on the reference solid, which may be expressed in several essentially equivalent ways such as the statistical film thickness ($t$), standard reduced adsorption ($\alpha_s$), or surface coverage ($\theta_s$). In the case where adsorption on both solids proceeds via the same mechanism, that is, via multilayer adsorption, the comparative plot is linear in the whole pressure range. When the solid under study exhibits micropores, the presence of the latter manifests itself in enhanced low-pressure adsorption. Consequently, the initial part of the comparative plot (that is, the region of low pressures or, equivalently, low values of $t$, $\alpha_s$, $\theta_s$, or similar quantities, which are increasing functions of pressure) exhibits a sharp increase and then levels off at higher pressures, after micropores are filled with condensed adsorbate. Such a comparative plot can be used to evaluate the micropore volume and the external surface area (that of macropores and mesopores) [17, 19] or even the micropore size [22]. If the solid under study contains mesopores (or macropores and mesopores), adsorption in them initially proceeds via multilayer formation (the same way as on the macroporous reference), but capillary condensation takes place at higher relative pressures. Consequently, the initial part of the comparative plot is linear, but then the plot exhibits an upward deviation from linearity in the capillary condensation region and levels off when the mesopores are already filled with the condensed adsorbate [17, 22, 25-32]. When both micropores and mesopores are present, the shape of the comparative plot is more complicated and reflects the deviations from linearity due to both micropore filling and capillary condensation.

It was also found that the obtained $\alpha_s(p/p_0)$ and film thickness curve $t (p/p_0)$ can be accurately represented in the relative pressure range from 0.1 to 0.95 by the Harkins-Jura equation of the following form [27]:

$$\alpha_s(p/p_0) = 0.1385 \times \left( \frac{60.65}{0.03071 - \log(p/p_0)} \right)^{0.3968} \quad \text{eq.(3.3.16)}$$
and therefore,

\[
t(p/p^0) = 0.1 \left( \frac{60.65}{0.03071 - \log(p/p^0)} \right)^{0.3968}
\]

eq (3.3.17)

It is worthy to note that the film thickness \( t(p/p^0) \) obtained by using the eq. (3.3.17) as been used to calculate the pore size distributions by Kruk, et al. [27].

Clearly, if the isotherm under test is identical in shape with that of LiChrosphere Si-1000, the \( \alpha_s/t \)-plots must be a straight line passing through the origin, suggesting the absence of micropores and mesoporous pores. Otherwise, if there are micropores, the straight line will intersect at y-axis above zero because of more pickup of N\(_2\) in micropores.

3.3.5 \( \beta_s \)-plot analysis

In section 3.3.4, how to characterise the microporosity of mesoporous silica materials using \( \alpha_s \)-plots method was introduced. However, instead of using \( \alpha_s \) method gas adsorption volume can also be plotted against \( \beta_s = [\ln(0.4)/\ln(p/p^0)]^{(1/2.7)} \), which is equivalent to \( \alpha_s \) for a hypothetical nonporous adsorbent that undergoes adsorption according to Frenkel-Halsey-Hill (FHH) theory [8, 33, 34]. Since this relationship is valid over a wide range of relative pressures, \( 0.003 \leq p/p^0 \leq 0.994 \) [34], the substitution of \( \beta_s \) for \( \alpha_s \) should be valid over the range of pressures examined in this case. In this section, how to quantitatively assess the microporosity, mesoporosity, mesopore surface area, mean mesopore size will be discussed.
The $\beta_s$ analysis for pure mesoporous silica synthesized is shown in Figure 3.3.6. It has 4 different regions: (1) a curved, low-pressure adsorption region AB section due to adsorption in micropores with the pore size less than 2nm and small mesopores, normally $\beta<0.7$ in this section; (2) BC, a linear region corresponding to multilayer adsorption in relatively larger mesopores and on the external surface of the material; (3) CD section, representing the capillary condensation in the primary mesopores corresponding with steep inflection in the isotherm; (4) DE section (linear), which can be attributed to the multilayer adsorption on the external surface of the material. The following calculations are focusing on the second and fourth linear section in the $\beta_s$ plot.

The size of the primary mesopores can be determined from the $\beta_s$ plot by the $4V/A$ method as follows. Here, a hypothesis is made: the total surface area just includes the mesoporous surface and the microporous surface area considering small proportion of the outer surface area in the whole surface area. A linear fit to region 2 has the form:

\[
y = 219.3 \beta_s + 91.6
\]

Figure 3.3.7 $\beta_s$ plot analysis for pure siliceous mesoporous silica.

\[
y = 11.03 \beta_s + 606
\]

\[
A_{\text{meso}} = 535 \text{ m}^2/\text{g}
\]

\[
A_{\text{micro}} = 928 - 535 = 393 \text{ m}^2/\text{g}
\]

\[
D = 5.95 \text{ nm}
\]
Chapter 3: Characterization of mesoporous materials

\[ V_{ads} = m_{\text{nonmicro}} \beta_s + V_{\text{micro}} \]

and a linear fit to region 4 has the form: \( V_{ads} = m_{\text{ext}} \beta_s + V_{\text{meso}&\text{micro}} \)

where \( V_{ads} \) is the N\(_2\) volume adsorbed, \( m_{\text{nonmicro}} \) and \( m_{\text{ext}} \) are the slope of the region 2 and 4, respectively. \( V_{\text{micro}} \) and \( V_{\text{meso}&\text{micro}} \) correspond to the intercepts of two lines on the axis y. As shown in Figure 3.3.7, two linear equations were given. In this case, \( m_{\text{nonmicro}}, V_{\text{micro}}, m_{\text{ext}}, V_{\text{meso}&\text{micro}} \) are equal to 11.03, 606, 219.3, and 91.6, respectively.

The mesopore volume, \( V_{\text{meso}} \), is equal to \( c (V_{\text{meso}&\text{micro}} - V_{\text{micro}}) \)

where \( c = 0.001547 \) is the factor used to convert the amount of nitrogen gas adsorbed at STP to the liquid volume at 77 K. The mesopore surface area, \( A_{\text{meso}} \), is equal to \( A_{\text{ref}} (m_{\text{nonmicro}} - m_{\text{ext}})/m_{\text{ref}} \)

where \( A_{\text{ref}} \) is the surface area of an appropriate nonporous reference material and \( m_{\text{ref}} \) is the slope of the \( V_{ads} \) vs \( \beta_s \) plot for that material. If the \( c_{\text{ref}} = A_{\text{ref}}/m_{\text{ref}} \), then \( A_{\text{meso}} = c_{\text{ref}} (m_{\text{nonmicro}} - m_{\text{ext}}) \) = 2.57. The diameter of the primary mesopores, \( D_{\text{meso}} \), is equal to \( 4V_{\text{meso}}/A_{\text{meso}} \).

So from Figure 3.3.7:

\[ A_{\text{meso}} = (219.3 - 11.03) \times 2.57 = 535 \text{m}^2/\text{g} \]

\[ V_{\text{meso}} = (606 - 91.6) \times 0.001547 = 0.8 \text{cm}^3/\text{g} \]

\[ D_{\text{meso}} = 4V_{\text{meso}}/A_{\text{meso}} = 5.95 \text{nm} \]

However, it is noteworthy to note that many studies have shown that the usual value for the molecular area of nitrogen adsorbed on silica, 16.2 Å [35], which is used to calculate the BET surface area, is too high due to the denser packing of nitrogen molecules that occurs on silica [36]. A more accurate value is 13.5 Å [35, 36]. Therefore, \( c_{\text{ref}} \), as indicated by Lukens et al. [37], should be 2.20, so that \( D_{\text{meso}} \) should be about 6.95nm.

3.4 Infrared spectroscopy

3.4.1 IR regions

The infrared (IR) region of the spectrum encompasses radiation with wave-numbers ranging from about 12800 to 10 cm\(^{-1}\) or wavelength from 0.78 to 1000 μm. From the
viewpoint of both application and instrumentation, the IR spectrum is conveniently divided into near-(wavelength 12800–4000 cm\(^{-1}\)), mid-(wavelength 4000–200 cm\(^{-1}\)), and far-IR (wavelength 200–10 cm\(^{-1}\)) radiation. Up to now, the majority of analytical applications have been confined to a portion of the mid-IR region extending from 4000 cm\(^{-1}\) to 400 cm\(^{-1}\).

### 3.4.2 Vibrations

Generally, IR radiation is not energetic enough to bring about electronic transitions. Absorption of IR radiation is thus confined largely to molecular species for which small energy difference exist between various vibrational and rotation states. When an asymmetric molecule (for example, hydrogen chloride molecule) having a dipole moment (such molecules polar) undergoes vibration, a regular fluctuation in dipole moment occurs. The field established can interact with the electrical field associated with radiation. If the frequency of the radiation exactly matches a natural vibrational frequency of this molecule, a net transfer of energy takes place that results in a change in the amplitude of the molecular vibration. Similarly, the rotation of asymmetric molecules around their centres of mass results in a periodic dipole fluctuation that can interact with radiation. No net change in dipole moment occurs during the vibration or rotation of homonuclear species such as O\(_2\), N\(_2\), or Cl\(_2\); consequently such compounds cannot absorb in the IR. The energy required to cause a change in rotation level is minute and corresponds to radiation of 100 cm\(^{-1}\) or smaller, whilst vibration energy levels in most cases correspond to mid-IR region (200–4000 cm\(^{-1}\)).

Figure 3.4.1 shows two types of molecular vibrations, stretching vibrations and bending vibrations. It can be see from this figure that a stretching vibration involves a continuous change in the interatomic distance along the axis of the bond between two atoms. Bending vibrations are characterised by a change in the angle between two bonds and are of four types: scissoring, rocking, wagging and twisting. All of the vibration types shown in Figure 3.4.1 may be possible in a molecule containing 3 or
more atoms. Additionally, interactions or coupling of vibrations may happen and incur changes in the characteristics of the vibrations involved.

![Diagram of molecular vibrations]

**Figure 3.4.1** Types of molecular vibrations. Note: + indicates motion from the page toward the reader; – indicates motion away from the reader.

### 3.4.3 Application of IR spectroscopy

IR spectroscopy finds widespread application to qualitative and quantitative analyses. Its single most use has been the identification of organic compounds whose mid-IR spectra are generally complex and provide numerous maxima and minima that are useful for comparison purposes (see Figure 3.4.2). In fact, in most cases, the mid-IR spectrum of an organic compound provides a unique fingerprint, which is readily distinguished from the absorption patterns of all other compounds; only optical isomers absorb in exactly the same way.
The general use of mid-infrared spectroscopy by chemists for identification of organic compounds began in the late 1950s. Identification of an organic compound from a spectrum of this kind is a two-step process. The first step involves determining what functional groups are most likely present by examining the group frequency region, which encompasses radiation from about 3600 cm\(^{-1}\) to approximately 1200 cm\(^{-1}\). Figure 3.4.2 shows the FTIR spectra of poly (methyl methacrylate) (PMMA). From this figure, it can be seen that several group frequencies are identified. A split peak at 2900 cm\(^{-1}\)-3000 cm\(^{-1}\), which corresponds to a C–H stretching vibration, indicates the presence of one or more alkane groups. Two peaks at 1380 cm\(^{-1}\) and 1450 cm\(^{-1}\) are also characteristic group frequency for C–H groups resulting from bending vibrations in PMMA molecules. Additionally, a broad peak at 3400 cm\(^{-1}\) indicates the O–H stretching vibrations of the water in PMMA and a strong peak at about 1730 cm\(^{-1}\) can be assigned to the C=O stretching vibrations.
The second step then involves a detailed comparison of the spectrum of the unknown with the spectra of pure compounds that contain all of the functional groups found in the first step. The fingerprint region, from $1200\text{cm}^{-1}$ to $600\text{cm}^{-1}$, is particularly useful, because small differences in the structure and constitution of a molecule result in significant changes in the appearance and distribution of absorption peaks in this region. Consequently, a close match between two spectra in the fingerprint region constitutes almost certain evidence for the identity of the compounds yielding the spectra. Most single bonds give rise to absorption bands at these frequencies; because their energies are about the same, strong interaction occurs between neighboring bonds. The absorption bands are thus composites of these various interactions and depend upon the overall skeletal structure of the molecule. Because of their complexity, exact interpretation of spectra in this region is seldom possible; on the other hand, it is this complexity that leads to uniqueness and the consequent usefulness of the region for final identification purposes. Figure 3.4.2 illustrates the unique character of IR spectra of PMMA in the fingerprint region from $600\text{cm}^{-1}$ to $1200\text{cm}^{-1}$, which distinguish the PMMA from other organic species.

Additionally, IR spectroscopy can also be used for quantitative analyses because of its high sensitivity. An important use of IR absorption spectroscopy is as a detector for gas chromatography, where its power for identifying compounds is coupled with the remarkable ability of gas chromatography to separate the components of complex mixtures.

In this project, the IR technique was also employed to identify the formation of nickel silicates and silica, based on the bands characteristic of constitutional hydroxyls groups. Hydroxyls groups on silica that are used for grafting titania will also be studied using IR technique before and after the grafting. IR will also be used to study the interactions of nickel or titania species with silica base with regard to the formation of Si-O-Ni or Si-O-Ti bonds.
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3.5 Raman spectroscopy

The phenomenon as Raman scattering was discovered in 1928 [38] and has become one of the most versatile spectroscopic tools to study the low-lying excitations of condensed matter systems. Raman spectra are intimately related to electronic transitions between vibrational levels of nuclei constituting the molecule. Figure 3.5.1 shows various regions of electromagnetic spectrum. As shown in the Figure 3.5.1, Raman and IR share the same portion in the whole range of electromagnetic spectrum: many vibrations therefore can be observed in both IR spectra and Raman spectra.

<table>
<thead>
<tr>
<th>NMR</th>
<th>ESR</th>
<th>Microwave</th>
<th>Raman, IR</th>
<th>UV, Visible</th>
<th>X-ray</th>
<th>γ-ray</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-4}$</td>
<td>$10^{-2}$</td>
<td>1</td>
<td>$10^{2}$</td>
<td>$10^{4}$</td>
<td>$10^{6}$</td>
<td>$10^{8}$</td>
</tr>
<tr>
<td>$10^{4}$</td>
<td>$10^{2}$</td>
<td>1</td>
<td>$10^{-2}$</td>
<td>$10^{-4}$</td>
<td>$10^{-6}$</td>
<td>$10^{-8}$</td>
</tr>
</tbody>
</table>

$\bar{\nu}$ (cm$^{-1}$)

$\lambda$ (cm)

Figure 3.5.1 Regions of electromagnetic spectrum.

An important advantage of Raman spectra over IR lies in the fact that water does not cause interference; indeed, Raman spectra can be obtained for aqueous solution. In addition, glass or quartz cell can be employed, thus avoiding the inconvenience of working with sodium chloride or other atmospherically unstable windows. Despite these advantages, Raman spectroscopy was not widely used by chemists for structural studies until lasers become available in the 1960s. Another deterrent to the general use of Raman spectroscopy was interference by fluorescence of the sample or impurities in the sample, which has now largely been overcome by the use of an IR laser source and Fourier transform spectrometers.

3.5.1 Mechanism of Raman and Rayleigh Scattering
Figure 3.5.2 Differences in the mechanism of Raman vs IR.

It is also easy to explain the origin of Raman by comparing with IR. As shown in Figure 3.5.2, IR measures the absorption of infrared light by the sample as a function of frequency. The intensity of IR absorption is governed by the Beer-Lambert law:

\[ I = I_0 e^{-\varepsilon cd} \]

Here, \( I \) and \( I_0 \) denote the intensities of the incident and transmitted beams, respectively, \( \varepsilon \) is the molecular absorption coefficient, and \( c \) and \( d \) are the concentration of the sample and the cell length, respectively. The origin of Raman spectra is different from that of IR spectra. In Raman spectroscopy, the sample is irradiated by intense laser beams in the UV-vis region \( (V_0) \), and the scattered light is usually observed in the direction perpendicular to the incident beam (see Figure 3.5.2). There are two types of light scattering: Rayleigh scattering, is strong and has the same frequency as the incident beam \( (V_0) \), and the other, called Raman scattering, is very weak and has frequencies \( V_0 \pm V_m \). \( V_m \) is a vibrational frequency of a molecule \( (V_0 + V_m \) and \( V_0 - V_m \) are called the Stokes and anti-Stokes lines, respectively). Under normal conditions, although they give the same information, the Stokes lines are stronger than the anti-Stokes lines. It is customary to measure only the Stokes line in Raman spectroscopy. Therefore, what is measured in the Raman spectroscopy is vibrational frequency \( (V_m) \) as a shift from the incident beam frequency \( (V_0) \) [39].
Figure 3.5.3 Comparison of Raman and IR spectra. (Courtesy Perkin-Elmer Cor., Norwalk, CT.)

For a given bond, the energy shifts observed in a Raman experiment should be identical to the energies of its IR absorption bands, provided that the vibrational modes involved are active toward both IR and Raman scattering. Figure 3.5.3 illustrates the similarity of Raman and IR spectra; it is seen that several peaks with identical $\bar{v}$ and $\Delta \bar{v}$ values exist for two compounds. However, it is worthy to note that the relative size of the corresponding peaks is frequently quite different; moreover, certain peaks that occur in one spectrum are absent in the other.

When taking consideration of the different mechanisms of IR and Raman, it is not surprising to see above differences. IR absorption requires that a vibrational mode of the molecule have a change in dipole or charge distribution associated with it. Only then can radiation of the same frequency interact with the molecule and promote it to an excited vibrational state. In contrast, scattering involves a momentary distortion of the electron distributed around a bond in a molecule, followed by reemission of the radiation as the bond returns to its ground electronic state. In its distorted form, the molecule is temporarily polarized; that it, it develops momentarily an induced dipole, which disappears upon relaxation and reemission. That explains why Raman can also be used to examine homonuclear molecules such as $\text{O}_2$, $\text{N}_2$, or $\text{Cl}_2$, whilst IR cannot.
3.5.2 Instrumentation

Figure 3.5.4 shows a Schematic diagram of a typical dispersive Raman system [40]. Commercially available Raman spectrometers consist of five major components: excitation source (continuous wave gas laser); sample illumination and scattered light collection system; sample holder, monochromator or spectrograph; detection system (detector, amplifier and output devices).

The most widely used Raman source is probably a helium/neon laser, which operates in a continuous mode at a power of 50mW. Laser radiation is produced at 632.8nm. Several other lower-intensity non-lasing lines accompany the principal line and must be removed by suitable narrow-band filters or by making the distance between the
source and entrance slit large. Another excitation source is Argon-ion lasers with lines at 488 nm and 514.5 nm especially for applications required high sensitivity. Because the scattering intensity depends upon the fourth power of the frequency of the excitation source, the Argon line provides Raman lines that are nearly three times as intense as those excited by helium/neon source, given the same input power. The Nd:YAG laser that emits near-IR radiation at 1064 nm is finding more and more use as an excitation source. It has two major advantages over shorter-wavelength sources. The first is that it can be operated at much higher power (up to 50W) without causing photo-decomposition of the sample. The second advantage is that it is incapable of causing fluorescence.

Application of Raman spectroscopy in this project is driven by its extremely high sensitivity to crystallinity of titania. Raman bands at 140 cm⁻¹ (very strong) and at 395, 514, and 638 cm⁻¹ (weak) reveal that the minimum amount of anatase phase which can be detected by this method corresponds to 0.5%, if a single channel analyzer is used [41]. Thus, Raman spectroscopy is used in this project to obtain useful information on the crystallinity of synthesized titania containing mesoporous silica.

3.6 X-ray photoelectron spectroscopy

In certain areas of science and engineering, the composition of a surface layer of a solid that is a few Angstroms to a few tens of Angstrom units in thickness is of greater importance than is the bulk composition of the materials. Fields in which surface properties are of primary importance include; heterogeneous catalysis, semiconductor thin-film technology, corrosion and adhesion studies, and activity of the behaviour and functions of biological membranes. Electron beams are ideally suited for such studies because under certain circumstances electrons can penetrate, or escape from only the outermost layers of a solid. For instance, X-ray electron beam will typically penetrate ~1μm of solid and only electrons in ~10nm layers can escape and be detected.
Followed by the appearance of electron spectrometers, an explosive growth in the number of publications devoted to electron spectroscopy occurred [42]. The most common type of electron spectroscopy, which is based upon irradiation with X-radiation, is called Electron Spectroscopy for Chemical Analysis (ESCA) or X-ray Photoelectron Spectroscopy (XPS).

![Figure 3.6.1 schematic representation of X-ray photoelectron spectroscopy][43].

The use of XPS for chemical analysis was pioneered by a Swedish Physicist K. Siegbahn, who subsequently received the 1981 Nobel Prize for his work [44]. Figure 3.6.1 is a schematic representation of XPS process. Here, the three lower lines, labelled $E_b$, $E_b'$, and $E_b''$, represent energies of the inner shell K and L electrons. The upper three lines represent some of the energy levels of the outer shell or valence electron. As shown in Figure 3.6.1, one of the photons of a monochromatic X-ray beam of known energy $h\nu$ displaces an electron $e^-$ from a K orbital $E_b$. The reaction can be represented by:

$$A + h\nu \rightarrow A^{**} + e^-$$

where $A$ can be an atom, a molecule, or an ion and $A^{**}$ is an electronically excited ion with a positive charge greater than that of $A$. 

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The kinetic energy of the emitted electron $E_k$ is measured in an electron spectrometer. The binding energy of the electron $E_b$ can then be calculated by means of the equation

$$E_b = h\nu - E_k - w$$

In this equation, $w$ is the work function of the spectrometer, a factor that corrects for the electrostatic environment in which the electron is formed and measured.

Figure 3.6.2 X-ray photoelectron spectrum of Nickel-containing silica

Figure 3.6.2 shows the X-ray photoelectron spectrum consisting of a plot of electron counting rate as a function of binding energy $E_b$. In this Figure, peaks for Oxygen, Si, and Ni are present, the large background count arises because associated with each characteristic peak is a tail due to ejected electrons that have lost part of their energy by inelastic collisions within the solid sample. It is evident from Figure 3.6.2 that XPS provides a means of qualitative identification of the elements present on the surface of solids. XPS is also extensively used to investigate the composition from the first 10nm. More details about the quantitative analysis [45] will not be discussed further here.
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XPS will be used in this project for characterising the nickel and titania functionalized mesoporous silica because it allows the determination of the chemical state of the elements of the solid surface including the oxidation state and a description of electronic interactions with neighbouring elements.

3.7 UV-vis absorption

The absorption of ultraviolet (UV) or visible radiation by an atom or molecular species M can be considered to be a two-step process, the first of which involves electronic excitation as shown by the equation

\[ M + h\nu \rightarrow M^* \]

The product of the reaction between M and the photon hv is an electronically excited species symbolized by \( M^* \), which will undergo several relaxation processes. The most common type of relaxation involves conversion of the excitation energy to heat; that is,

\[ M^* \rightarrow M + \text{heat} \]

The absorption of UV or visible radiation generally results from excitation of bonding electrons; as a result, the wavelengths of absorption peaks can be correlated with the types of bonds that exist in the species under study. Molecular absorption spectroscopy is therefore valuable for identifying functional groups in a molecule. More important, however, are the applications of UV and visible absorption spectroscopy to the quantitative determination of compounds containing absorbing groups. Three types of electronic transitions are recognize involving (1) \( \pi, \sigma, \) and \( n \) electrons, (2) \( d \) and \( f \) electrons, and (3) charge-transfer electrons.

UV-visible spectrophotometry has somewhat limited application for qualitative analysis, because the number of absorption maxima and minima is relatively small. Thus, unambiguous identification is frequently impossible. However, UV absorption spectroscopy is one of the most useful and widely used tools available to the chemist for quantitative analysis. Important characteristics of spectrophotometric and photometric methods include (1) wide applicability to both organic and inorganic...
system, (2) typical sensitivities of $10^{-4}$ to $10^{-5}$ M (this range can often be extended to $10^{-6}$ to $10^{-7}$ M by certain modifications [46]), (3) moderate to high selectivity, (4) good accuracy (typically, relatively uncertainties of 1-3% are encountered although with special precautions, errors can be reduced to a few tenth of a percent), and (5) ease and convenience of data acquisition.

The first steps in a spectrophotometric and photometric analysis involve the establishment of a working condition and preparation of calibration curve relating concentration to absorbance because the concentration is linearly proportional to absorption according to the Beer's law (see section 3.5.1). Spectrophotometric absorbance measurements are ordinarily made at a wavelength corresponding to an absorption peak, because the change in absorbance per unit of concentration is greatest at this point. After deciding upon the conditions for the analysis, it is necessary to prepare a calibration curve from a series of standard solutions.

In this project, UV-spectroscopy will be used to determine the concentration of salicylic acid and phenol in water. Additionally, concentration of oestrogen can also be determined easily by this method.

3.8 UV-vis-Diffuse Reflectance spectroscopy

In section 3.7, UV-vis absorption spectroscopy and its quantitative application for chromophores were introduced, which only involve the absorption of UV-vis irradiation. However, for systems such as solids, semi-solids, or turbid liquids, where scattering and reflection may happen, it is often impossible to get their UV-vis absorption spectra. In this case, the Beer-Lambert law does not apply, because the nearly all the incident radiation is scattered out of the acceptance angle of the detector and the path length, $d$, is no longer determined. Fortunately, UV-vis diffuse reflectance (UV-DRS) spectroscopy makes possible the extraction of the absorption properties from the reflected light instead of transmitted light.
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Figure 3.8.1 Schematic diagram of a diffuse reflectance spectrophotometer with integration sphere.

In a DRS spectrum the ratio of the light scattered from an infinitely thick layer and the scattered light from an ideal non-absorbing reference sample is measured as a function of the wavelength \( \lambda \). Figure 3.8.1 shows a schematic overview of a diffuse reflectance spectrophotometer with integration sphere. As schematically illustrated in this figure, the illumination of powdered samples by incident radiation leads to diffuse illumination of the samples. The incident light is partially absorbed, partially scattered. The scattered radiation, emanating from the sample is collected in an integration sphere and detected.

\[
-\frac{dI}{dS} \times \frac{1}{\kappa \rho} = I - \frac{j}{\kappa}
\]

The basic equation for the phenomenological description of diffuse reflection is the radiation transfer eq.(3.8.1): where \( I \) is the incident light intensity of a given wavelength; \( dI/dS \) the change of the intensity within the path length \( dS \); \( \rho \) the density of the medium; \( \kappa \) an attenuation coefficient corresponding with the total radiation loss due to absorption and scattering; \( j \) is the scattering function. Eq. (3.8.1) can be solved by introducing simplifications which are related with easily attainable experimental conditions. These ideas, first suggested by Schuster and later on further developed by Kubelka and Munk, simplify the solution of the radiative transfer Eq. (3.8.1), known as the Schuster-Kubelka-Munk (SKM) theory [47].
In this theory, the incident and scattered light flux are approximated by two fluxes $I$ and $J$ perpendicular to the surface of the powdered sample, but in the opposite direction. This is illustrated in Figure 3.8.2. It can be seen from this figure that, $I$ is the flux of monochromatic diffuse illumination, whereas $J$ is the flux of diffusively scattered light. If the sample is infinitely thick, the diffuse reflection of the sample ($R_I$) is related to an apparent absorption ($K$) and apparent scattering coefficient ($S$) via the S-K-M or K-M function:

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = K \frac{S}{S}$$

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = K \frac{\alpha C_{\text{TMI}}}{S}$$

When at a given wavelength $\lambda$, $S$ is constant, Eq. (3.8.3) gives a linear relation between $F(R_\infty)$ and the TMI concentration, $C_{\text{TMI}}$. The coefficients $\alpha$ is proportionality constants. Therefore, K-M equation allows the quantitative determination of TMI concentration in the samples.
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DRS is a particularly suitable technique for studying the TMIs because it measures both their d-d transitions and charge transfer bands. This is illustrated in Table 3.8.1 for some reference chromium compounds [48]. It is clearly shown in this table that the number, wavelength and intensity of the d-d bands depend on the oxidation state (Cr$^{2+}$ vs Cr$^{3+}$) and coordination environment (octahedral, tetrahedral, etc.), whereas the charge transfer transitions of the type O→Cr$^{6+}$ (d$^0$) are responsible for the intense yellow-orange color of calcined chromium oxide catalysts.

### Table 3.8.1 bands of DRS spectra of some reference Cr-compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Coordination geometry and oxidation state</th>
<th>Absorption bands (nm)*</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_2$CrO$_4$ (solution)</td>
<td>Ta, Cr$^{6+}$</td>
<td>440 (sh, yw), 370 (s), 275 (s)</td>
<td>Yellow</td>
</tr>
<tr>
<td>K$_2$CrO$_4$ (solid)</td>
<td>Ta, Cr$^{6+}$</td>
<td>459 (s), 340 (s), 265 (s), 229 (s)</td>
<td>Yellow</td>
</tr>
<tr>
<td>K$_2$Cr$_2$O$_7$ (solution)</td>
<td>Ta, Cr$^{6+}$</td>
<td>440 (w), 352 (s), 255 (s)</td>
<td>Orange</td>
</tr>
<tr>
<td>K$_2$Cr$_2$O$_7$ (solid)</td>
<td>Ta, Cr$^{6+}$</td>
<td>526 (s, w), 332 (s), 263 (s), 229 (s)</td>
<td>Orange-red</td>
</tr>
<tr>
<td>Cr(NO$_3$)$_3$.9H$_2$O (solution)</td>
<td>Octa, Cr$^{3+}$</td>
<td>575 (s), 410 (s), 303 (s)</td>
<td>Green</td>
</tr>
<tr>
<td>Cr(NO$_3$)$_3$.9H$_2$O (solid)</td>
<td>Distorted Octa, Cr$^{3+}$</td>
<td>575 (s), 410 (s), 304 (s), 263 (sh)</td>
<td>Green</td>
</tr>
<tr>
<td>Cr(H$_2$O)$_6$Cr$^{6+}$ (solution)</td>
<td>Octa, Cr$^{6+}$</td>
<td>769 (s)</td>
<td>Blue</td>
</tr>
<tr>
<td>Cr$_2$O$_3$ (solid)</td>
<td>Distorted Ta, Cr$^{2+}$</td>
<td>1430 (s)</td>
<td>Blue</td>
</tr>
<tr>
<td>Cr$_2$O$_3$ (solid)</td>
<td>Distorted Octa, Cr$^{3+}$</td>
<td>714 (sh), 645 (sh), 595 (s), 461 (s), 351 (s), 274 (s)</td>
<td>Green</td>
</tr>
</tbody>
</table>

*; s: strong; m: medium; w: weak; yw: very weak; sh: shoulder; br: broad.

![Figure 3.8.3 Plots of (F(R$_o$)*hv)$^{1/2}$ against photo energy (hv).](image)

In this project, UV-vis DR technique is used to examine the oxidation state and local symmetry of Ni and Ti centres incorporated into the mesoporous silica. Importantly, measurements of the bandgap ($E_g$) energy of semiconductor oxides can also be carried
out, e.g. the TiO₂ phases incorporated in the mesoporous silica. Titania is a semiconductor oxide with an easily measured optical bandgap [49, 50]. Figure 3.8.3 shows the plots of \((F(R_\infty)*h\nu)^{1/2}\) against photo energy \((h\nu)\). The band gap energy \((E_g)\) for allowed transitions was determined by finding the intercept of the straight line in the low-energy rise of \([F(R_\infty)h\nu]^{1/2}\) against \(h\nu\) (near the absorption edge, the absorption coefficient, \(\alpha\) is proportion to \([F(R_\infty)h\nu]^{1/2}\), where \(F(R_\infty)\) is Kubelka-Munk function (eq. (3.8.2)) and \(h\nu\) is the incident photon energy [51, 52]. From Figure 3.8.3, the bandgap energy can be determined to be 3.75ev.

References


Chapter 3: Characterization of mesoporous materials


Chapter 4 Ni-containing mesoporous silica systems

4.1 Introduction

Silica-supported nickel catalysts have been widely studied and used due to their very high catalytic activity in hydrogenation, hydrotreating and stream-reforming reactions [1]. Especially, the discovery of the family of M41S by Mobil scientists in 1992 provides a new opportunity to combine the mesoporous silica and catalytically active nickel.

The most common method for the synthesis of nickel-containing mesoporous silica is by impregnation. In this method, mesoporous catalyst supports are impregnated by nickel salt solutions, such as nickel nitrate [2-7], nickel bromide [8], and nickel citrate [9]. The disadvantage of this method is that high loadings of Ni exceeding 5wt.% often lead to loss of the BET surface area or even blockage of mesochannels by large Ni (NiO) particles. As reported by Rodríguez-Castellón et al. [6], 48% of BET surface area was left after 14.9wt % Ni was incorporated and large nickel oxide particles were located on the external surface. When 5wt% nickel was loaded into MCM-41, only about 73% of total surface area remained [7]. Even with only 1.5wt% Ni loading into AlMCM-41, NiO particles of ~2nm were formed in the mesochannels [8].

Therefore, an alternative way to introduce nickel species into the mesoporous silica is adding Ni salts, like NiCl2, Ni(NO3)2, into the synthesis mixture, followed by the hydrothermal treatment, called direct synthesis method (DS method). However, it is difficult to load high amount of nickel without damaging the mesostructures using this method [10-12]. For example, with very low nickel loading (<1.5wt %), distinct condensation in mesopores was not observed in N2 sorption measurement [12]. So far, to our knowledge, no reports have been published on synthesis of MCM-41-type silica with higher nickel content than 3.6wt.% using the DS method [11]. Rapid precipitation of nickel ions in basic conditions does not allow full interaction with the template
molecules, which results in the low loading into the mesophases and formation of extra-framework NiO after calcination.

In this Chapter, a modified DS method for the synthesis of MCM-41-type mesoporous silica with high nickel content was developed. In this method, 'TEOS-seizing nickel species' co-hydrolyzes and co-condenses with TEOS during the hydrothermal treatment for building up mesostructures templated by cationic surfactant. This method has been proved to be effective for incorporation of higher amounts of nickel into mesophases.

Furthermore, the mesostructures of such nickel-containing mesoporous silica were examined by techniques such as low-angle XRD, TEM, N2-sorption. EDX measurements were performed for determination of nickel content and Ni dispersions. Wide-angle XRD, XPS, FTIR, UV-vis-DRS were employed to characterise the nickel species loaded in the mesoporous silica.

4.2 Experimental

4.2.1 Materials

Cetyltrimethylammonium bromide (CH3(CH2)15N(CH3)3+Br−, C16TMABr or CTAB), ethylene glycol (anhydrous, designated as EG), mesitylene, tetraethyl orthosilicate (TEOS, 98%), nickel (II) nitrate hexahydrate, hydrogen chloride (HCl, 37%) were purchased from Aldrich (UK). Absolute ethanol, sodium hydroxide was purchased from Fisher (UK). All chemicals were used as received without further purification.

4.2.2 Synthesis of nickel-containing mesoporous silica

4.2.2.1 Synthesis of mesoporous silica

0.7g CTAB was dissolved in 31g distilled water. 5g solution of NaOH (2M) was dropped into above solution. 4.25ml (≈ 0.02mol) TEOS was added dropwise. This solution was stirred moderately at 297K overnight. Then the mixture formed was kept statically at 370K for 144 hours. The white products were washed, filtered for
three times, and then air-dried at 333K overnight. The following step of calcination was carried out from the room temperature to 823K with the heating rate of 1K per minute and was kept for 6 hours, followed by cooling down to room temperature naturally. All samples obtained were stored in sealed bottles.

4.2.2.2 Synthesis of Ni-containing mesoporous silica

Typically, for the synthesis of MNi-11 (Ni-containing mesoporous silicas were denoted as MNi-XX, XX stands for the nominal weight percent of nickel, if no specification, MNi-XX always refers to the calcined one):

Solution A: 0.6g nickel (I) nitrate hexahydrate was dissolved into 3.5mL ethylene glycol. The solution was heated at 363K for 10 hours with stirring in open air and then 4.25mL TEOS was added dropwise and sealed in the bottle. The formed gel was aged at 363K for 10 hours with stirring.

Solution B: 0.7g CTAB was dissolved in 31g distilled water, and then 5g solution of NaOH (2M) was added dropwise into above one. Solution A was added to solution B dropwise. The final pH value was adjusted to ≈11.0 and then the gel was aged at 298K overnight with moderate stirring. The mixture formed was then kept statically at 370K for 120 hours. The pH value of the final mixture was adjusted to ≈ 2.0 using HCl. The slightly green products were washed, filtered for three times, air-dried at 333K overnight. The following step of calcination was carried out from the room temperature to 823K with the heating rate of 1K per minute and kept at 823K for 6 hours, followed by cooling down to room temperature naturally. All the samples obtained were stored in sealed bottles.

4.2.2.3 Synthesis of MNi-11-D

In order to compare with MNi-11, Ni-containing mesoporous silica was synthesized using unmodified DS method (designated as MNi-11-D). The starting composition is the same as MNi-11.
Solution A: 0.7g CTAB was dissolved in 31g distilled water, and then 5g solution of NaOH (2M) was added dropwise to above one. 0.6g nickel (II) nitrate hexahydrate and 3.5mL ethylene glycol was added to solution A. And then 4.25mL TEOS was added dropwise and sealed in the bottle. The final pH value was adjusted to ≈11.0. The obtained mixture was aged at 298K overnight with moderate stirring followed by keeping at 370K for 120 hr statically. The pH value of the final mixture was adjusted to ≈2.0 using HCl. The following steps are the same as those for MNi-11. Table 4.2.1 gives the summarisation of synthesis selecting MNi-11 and MNI-11-D as examples.

Table 4.2.1 Synthesis process for MNi-11 and MNI-11-D.

<table>
<thead>
<tr>
<th></th>
<th>MNI-11</th>
<th>MNI-11-D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni(NO₃)₂ 6H₂O dissolved in EG at 363K, stirring for 10hr</td>
<td>‘simple’ mixture of Ni(NO₃)₂ 6H₂O, EG and TEOS</td>
</tr>
<tr>
<td>2</td>
<td>TEOS added to above solution at 363K, stirring for 10hr</td>
<td>Templating process by CTAB solution</td>
</tr>
<tr>
<td>3</td>
<td>Templating process by CTAB</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Calcination at 823K for 6hr</td>
<td>Calcination at 823K for 6hr</td>
</tr>
</tbody>
</table>

4.2.2.4 Synthesis of MNI-5, 15
Mesoporous silica with different nickel content can also be synthesized by just using different amounts of nickel precursor and EG. For the synthesis of MNI-5 and MNI-15, nickel nitrate hexahydrate of 0.29g with 3.5ml EG and 1.0g with 4.5ml EG were used, respectively. The synthesis procedures are the same as MNI-11.

4.2.2.5 Reduction of calcined MNI-5, 11, 15
Reduction using H₂/N₂ (5%, v/v) was conducted at 773K or at 923K for 4hr with heating speed of 10K per min.

4.2.3 Instrumentation
X-ray powder diffraction (XRD) data were obtained on Bruker D8 diffractometer operated at 40kV, 40mA, using CuKα radiation (λ=0.1542 nm) with the increment of 0.02° for the efficient signal/noise ratio. The samples were mounted onto a holder with flat surface. The scanning started from 1° to 10° for characterization of the mesostructure and from 15° to 80° for the crystalline phase and elements analysis.

Transmission electron microscopy (TEM) images were obtained on a JEOL 2000 FX or a Philips Tecnai transmission electron microscope operated at 200 kV. The powder was supported on holey carbon films mounted on 200 meshes, 3mm TEM copper grids. Images from the edges were recorded under appropriate focus conditions. In some images, the light areas correspond to a lack of scattering materials (pores), and the dark areas are concentrations of scattering matter (walls).

Element analysis was performed using an energy dispersive X-ray spectroscopy (EDX) and operated at 200 kV. EDX spectra were analyzed using the K lines of Si and Ni for NiO-containing silica and Si.

X-ray Photoelectron Spectroscopy (XPS) measurements were performed on an Escalab MKI spectrometer equipped with a hemispherical electron analyzer and an Al-Kα X-ray exciting source (1486.6eV, 8kV, 20 mA). The samples were placed in a small copper cylinder and mounted on a transfer rod placed in the pre-treatment chamber of the instrument. Binding energies (BE) were referenced to Si2p at 103.4eV with the accuracy of ±0.2eV. The powders were degassed at room temperature for 3 hours before mounting on the sample holder. For the samples recorded with take-off angle of 30 degrees, they are pressed into pellets with smooth surface in advance. The binding energy and atomic concentrations were calculated from the XPS results using the total integrated peak areas of Ni 2p, Si 2p and O 1s regions. The spectra were smoothed, and nonlinear Shirley-type background was subtracted. Deconvolution was carried out using the theoretical XPS bands—20% Lorenz and 80% Gauss, via a least squares algorithm. An XPS peak fitting software of XPSPEAK4.1 was used.
atomic concentration ratios were calculated by correcting the intensity ratios with theoretical sensitivity factors proposed by the manufacturer.

BET surface area was calculated from nitrogen adsorption isotherms at 77K using a micromeritics ASAP 2010 surface analyser, and a value of 0.164nm$^2$ as the cross-section of the nitrogen molecule. The calculation of the pore sizes distribution uses BJH model described in Chapter 3. The surface area was obtained by using BET model (see Appendix I).

Fourier transform infrared spectroscopy (FTIR) was collected on a Mattson 3000 FTIR spectrometer using the mixtures of the sample and KBr. Spectra were acquired at 4cm$^{-1}$ resolution and averaged over 64 scans.

UV-vis Diffuse Reflectance Spectra (UV-vis DR spectra) were collected on Perkin Elmer UV/Vis spectrometer (Lambda Bio 40) in the range from 250nm to 600nm. Reflectance data were converted to $f(R_{\infty})$ values using the Kubelka-Munk equation.

Temperature Programmed Reduction (TPR) was carried out with heating speed of 10K/min Temperature range covered from 373K-1223K. Flow rate of H$_2$ in Ar (5% v/v) was controlled at 25ml/min. H$_2$ concentration was monitored by mass spectroscopy.
4.3 Modified direct synthesis method

As above mentioned, the DS method for the introduction of nickel species into the mesoporous silica involves the addition Ni salts, like NiCl₂, Ni(NO₃)₂, into the synthesis mixture, followed by the hydrothermal treatment. The loading of nickel can be accomplished during the synthesis of mesoporous silica. This means the simplification of synthesis procedures compared with post synthesis method. Moreover, no blockage of mesopores happens because the nickel species are loaded into the silica frameworks. However, the key difficulty is the low loading using DS method, provided that quality mesostructures need to be retained upon loading of nickel [10-12]. No reports have been published on synthesis of MCM-41-type silica with higher nickel content than 3.6wt.% using the DS method [11]. It is believed that the rapid precipitation of nickel ions in basic conditions does not allow full interaction with the template molecules, which results in the low loading into the mesophases and formation of extra-frameworks NiO after calcination. Possible solution to this problem could be to restrict the formation of bulk NiO and take advantage of the interaction between silica species and template molecules.

In the modified DS method, ‘TEOS-seizing nickel species’ co-hydrolyzes and co-condenses with TEOS during the hydrothermal treatment for building up mesostructures templated by cationic surfactant, CTAB. This method can guarantee the full interaction with CTAB molecules to build mesostructures. In the calcined samples, nickel species can be dispersed in the silica frameworks homogeneously. The modification process can be described using below equation:

\[
2(C_2H_5O)_4Si + (CH_2O)_2Ni \rightarrow (C_2H_5O)_3Si-O-Ni-O-Si(C_2H_5O)_3 + (C_2H_5OCH_2)_2
\]

Cyclic nickel glycoxide ((CH₂O)₂Ni) can be generated by dissolution of nickel hydroxide into ethylene glycol at 353K [13]. After adding the ethyl silicate, ethylene glycol diethyl ether and Ni-O-Si bonds can be formed [13, 14]. It is believed that the
connection of nickel ions with TEOS makes the co-hydrolysis and co-condensation occur at molecular level so that the homogeneous dispersion of the Ni in the frameworks of silica can be realized. This allows the incorporation of high amount of nickel into the silica frameworks. How effective this method is to load a high amount of nickel into the mesoporous silica and results of various characterization techniques will be discussed below in detail.
4.4 Ni-containing mesoporous silica systems

Many characterization techniques have been used to study the nickel containing mesoporous silica. These techniques provide the understanding of the mesostructural ordering, nickel dispersion, surface area and porosity, chemical state and interaction with silica matrix and coordination of Ni(II) centres in the silica matrix.

4.4.1 Mesostructural ordering of nickel-containing mesoporous silica

Using the modified DS method, Ni-containing mesoporous silica can be prepared. Through this method, mesoporous silica with different amounts of nickel can be achieved. Five kinds of nickel-containing mesoporous silica, MNi-5, 11, 15, 20 and 25 were synthesized. The structural parameters for these samples are shown in Table 4.4.1.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ni wt.%</th>
<th>D-spacing (nm)(^c)</th>
<th>Pore size (nm)(^d)</th>
<th>S.S.A (m(^2)/g)(^e)</th>
<th>Pore volume(cm(^3)/g)(^f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MNi-5</td>
<td>5.8(^b)</td>
<td>3.81</td>
<td>3.6</td>
<td>844</td>
<td>0.73</td>
</tr>
<tr>
<td>MNi-11</td>
<td>11.8(^a)</td>
<td>3.98</td>
<td>3.4</td>
<td>868</td>
<td>0.73</td>
</tr>
<tr>
<td>MNi-15</td>
<td>14.7(^a)</td>
<td>4.29</td>
<td>3.6</td>
<td>875</td>
<td>0.92</td>
</tr>
<tr>
<td>MNi-20</td>
<td>20.3(^b)</td>
<td>4.83</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>MNi-25</td>
<td>&gt;25</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

a: results obtained from the EDX equipped with TEM; b: results obtained from EDX equipped with SEM; c: calculated from the results of XRD by Braggs Equation; d: pore size is the most probable distributed pore diameter derived from the calculation of pore size distributions; e: S.S.A means specific surface area (BET); f: pore volume was calculated at a single point at p/p\(^0\)=0.9814, except the MNi-11, which is at p/p\(^0\)=0.969; g: dashes inserted indicate samples where frameworks collapsed, data not appropriate.
Figure 4.4.1 XRD patterns for the (A) as-synthesized and (B) calcined Mn-5.
Figure 4.4.2 XRD patterns for the (A) as-synthesized and (B) calcined MNi-11.
Figure 4.4.3 XRD pattern for the calcined MNi-15.

Figure 4.4.4 XRD patterns for (1) as-synthesized MNi-25, (2) as-synthesized MNi-20, and (3) calcined MNi-20.
XRD is a key method for the identification of the mesophases obtained. Figure 4.4.1 shows the low angle XRD pattern for the as-synthesized and calcined MNi-5. Apparently, the XRD patterns for as-synthesized and calcined MNi-5 give the expected peaks, indexed on a hexagonal unit cell with $a \approx 4.4$ nm at low angle $2\theta$ region, characteristic of MCM-41. Four peaks, indexable as (100), (110), (200), and (210) reflections associated with $p6mm$ hexagonal symmetry, reveal hexagonally arranged mesopores over long range. Furthermore, slight contraction from 3.91 to 3.81 nm can be seen, which is in accordance with that of pure mesoporous silica due to further condensation during the calcination. Additionally, the increase in $d_{100}$ from 3.38nm (MNi-00, mesoporous silica with 0wt.% of Ni) to 3.81nm for MNi-5 is normally the result of the incorporation of Ni into the silica walls. Similarly, Figure 4.4.2 shows the low angle XRD pattern for the as-synthesized and calcined MNi-11. Apparently, the XRD patterns for as-synthesized and calcined MNi-11 show the XRD reflections, characteristic of MCM-41-type mesostructures. At least 4 peaks, indexable as (100), (110), (200), (210) reflections and even more of (300), (220), (310), associated with $p6mm$ hexagonal symmetry, can be observed and attributed to the long range ordering of the mesopores. Slight contraction from 4.17 to 3.98nm can also be seen. Additionally, the increase in $d_{100}$ from 3.38nm for MNi-00 to 3.98nm for MNi-11 can be attributed to the incorporation of more Ni species into the silica frameworks than those into MNi-5. Apparently, the incorporation of nickel with content up to 11.8 does not lead to significant loss of low-angle XRD peaks. Comparing the low-angle XRD patterns for MNi-11 and MNi-5, the latter is more resolved, indicating the more regular and ordered mesostructures. These resolved peaks indicate the preservation of mesostructures and high ordering over long range upon incorporation of nickel species.

Figure 4.4.3 shows the XRD pattern for the calcined MNi-15. From this figure, it can be seen that, compared with MNi-5 and MNi-11, MNi-15 (14.7 wt.% of Ni) only shows one broad (100) reflection in the low-angle XRD pattern. Such lose in resolution suggests the deterioration of mesostructures upon increasing nickel
incorporated into the frameworks. The \(d_{100}\) further increases to 4.29 nm. Additionally, the broad (100) peak is due to the low ordering and regularity of mesopores arrangement. Further increase in the nickel content to 20 wt.% leads to almost disappearance of low-angle reflections in the XRD pattern as shown in Figure 4.4.4, it can be seen from this figure that, for samples with more than 25 wt.% of nickel, no distinguishable peaks in low angle region appear, indicating the complete collapse of the mesostructures.

Therefore, according to the low-angle XRD results, mesostructures are quite intact upon nickel loading up to 14.7 wt.%. Moreover, TEM photographs give further evidence and more information about the mesostructures.
As shown in Figure 4.4.5A, ordered mesopores over long range can be found for MNi-5. TEM micrographs of calcined MNi-11 (Figures 4.4.5B and C) also provide further evidence of the hexagonal mesostructures, which are inferior to that of MNi-5. This is in agreement with low-angle XRD results that the MNi-5 with low Ni loading possesses more regular and ordered mesostructures than MNi-11. In Figure 4.4.5C, the
slightly disordered mesostructures can be seen clearly. Such phenomena are often met when the incorporation of non-silicon atoms into the silica frameworks [15]. In Figure 4.4.5D, it can be seen that the mesostructures of MNi-15 with 14.7wt % nickel content get disordered. The more non-silicon atoms are loaded into the silica frameworks, the worse the mesostructures are. Therefore, the incorporation of higher amount of nickel into the silica frameworks leads to slight deterioration of mesostructures but which are still satisfactory, as confirmed by the N₂ sorption measurement. Bigger particles exceeding the mesopores were also not observed in TEM photographs.

<table>
<thead>
<tr>
<th>Spots</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni content wt. %</td>
<td>12.7</td>
<td>12.4</td>
<td>11.4</td>
<td>11.4</td>
<td>12.3</td>
<td>13.9</td>
<td>12.3</td>
</tr>
</tbody>
</table>

*Figure 4.4.6* TEM photograph of MNi-11 and the EDX results of selected areas.
Chapter 4 Ni-containing mesoporous silica systems

4.4.2 Nickel dispersion in mesoporous silica

Mesostructural ordering of nickel-containing mesoporous silicas with nickel content up to 14.7wt.% was examined by means of low-angle XRD and TEM measurements. For examining the nickel dispersion in mesoporous silica, EDX is an easy and direct technique.

<table>
<thead>
<tr>
<th>Areas</th>
<th>Spot 1</th>
<th>Spot 2</th>
<th>Spot 3</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni content wt.%</td>
<td>13.4</td>
<td>13.5</td>
<td>17.2</td>
<td>14.7</td>
</tr>
</tbody>
</table>

Figure 4.4.7 TEM photograph of calcined MNi-15 and the EDX results of selected areas.
Figures 4.4.6 and 4.4.7 give the EDX results on different areas of MNi-11 and MNi-15, respectively. The dispersion of nickel in MNi-11 is slightly more homogeneous that that in MNi-15. In Figure 4.4.7, the disordered mesophases are clear, which in accordance with the results of low-angle XRD, whereby only one (100) reflection is resolved with other high-angle peaks disappeared. This further proves the disordering of mesostructures upon higher nickel loading up to 15wt.% for MNi-15. Importantly, the nickel was further proved to be loaded into the silica frameworks (mesophases) instead of exclusively outside the mesophases, which is in agreement with the increasing d-spacing values observed in XRD measurements. Therefore, the possibility of forming the simple mixtures of nickel oxide and mesoporous silica can be excluded.

### 4.4.3 Surface area and porosity of Ni-containing mesoporous silica

Although the low-angle XRD and TEM have shown the ordering and quality of mesostructures, surface area and porosity of such mesoporous materials are still unknown. Therefore, N₂ sorption measurements were carried out to characterize the textural properties of these nickel-containing mesoporous silica.

BET surface areas of all samples are more than 800 m²/g, with the pore volumes exceeding 0.7 cm³/g, even though 14.7 wt.% Ni had been incorporated (shown in Table 4.4.1). These values are pretty high, indicating the opening of mesopores without collapse of mesostructures. In contrast, according to the published results, BET surface area often suffered significant decreases using the post-synthetic method, for example the impregnation method. BET surface area was reduced to 465 m²/g from 1051 m²/g after 6.9 wt.% Ni was filled into the channel of MCM-41 [16]. And similarly, BET surface area of mesoporous material with 7.77 wt% Ni decreased to 477 m²/g from 783 m²/g [17]. When 5 wt% nickel was loaded into MCM-41, total surface area decreased from 1082 to 796 m²/g [7]. When 14.9 wt% nickel was loaded into MCM-41, total surface area decreased from 851 to 346 m²/g [6]. In our case, no significant decrease of the surface area took place (see Table 4.4.1). BET surface areas are comparable to those of MCM-41 (if properly synthesized, BET surface area is in the
range of 800~1200m$^2$/g) when taking the weight increase due to the incorporation of nickel species into consideration. The high surface area for MNi-15, although its mesostructures get disordered, suggests the mesostructures be satisfactory with high nickel content up to 14.7wt%. Therefore, if the shortcoming of low loading of the DS method could be overcome, the advantage of the DS method over post-synthesis method is distinct in synthesizing high nickel-containing mesoporous silica with high surface area.

![Figure 4.4.8 N$_2$ adsorption data for samples of MNi-5 (shift by -60cm$^3$/g), 11(shift by +50cm$^3$/g) and 15 (shift by +200cm$^3$/g).](image)

From Figure 4.4.8, the isotherm for every sample exhibits the existence of mesoporosity. As expected, N$_2$ adsorption isotherms of type IV in character are shown in all samples. Due to the lack of desorption data on the hysteresis loops, it is impossible to further classify the isotherms. However, according to the results of MNi-11 and similar family of MCM-41, which were all synthesized using very dilute surfactant concentration (<3%, relative to water), usually only very little or no capillary hysteresis loops appeared. For all samples, inflections occur at $p/p^0 \approx 0.3$ and...
end at \( p/p^0 \approx 0.4 \), which are one of the peculiar features of M41s due to the primary mesopore filling step. The inflection at given \( p/p^0 \) values of MNI-11 and MNI-15 were not as steep as that of MNI-5. This can be attributed to the broad mesopore size distributions of mesopores because the capillary condensation pressure is an increasing function of the pore diameter [18, 19]. The pore size distributions will be discussed below. Such results about the broadening of pore size distributions are in agreement with results of XRD, TEM, whereby the disordered mesostructures are confirmed with high nickel loading.

![Graph showing pore distributions for samples: MNI-5, 11 and 15.](image)

Figure 4.4.9 Pore distributions for samples: MNI-5, 11 and 15.
**Chapter 4 Ni-containing mesoporous silica systems**

Figure 4.4.10 $\alpha$-plots (low region) curves for samples of MNI-5, 11 and 15.

Figure 4.4.11 $\alpha$-plots (whole region) curves for samples of MNI-5, 11 and 15.
The commonly used method for analyzing mesopore size distributions are the Barrett–Joyner–Halenda (BJH) model [20] with the corrected Kelvin equation for N\textsubscript{2} adsorption in cylindrical pores [19]. The calculations were performed from adsorption branches of isotherms using the relations between the pore diameter and the capillary condensation pressure derived by Halsey [21, 22]. The statistical film thickness curve suitable for these calculations was reported elsewhere [21, 22]. The pore size distributions are analyzed by this method. Figure 4.4.9 shows the pore distributions calculated by this method. Clearly, it can be seen from this figure that the mesopores are dominantly present within these samples. For all three nickel-containing mesoporous silica, no distinguished distributions of micropores can be found. However, the broadening of the pore diameter distribution indicates the deformation of hexagonal mesostructures. This can be attributed to incorporation of nickel into the mesophases.

Careful \(\alpha_s\)-plots analyses also prove the existence of mesopores. Nevertheless, the non-existence of micropores was also demonstrated. The \(\alpha_s\)-plots analysis was shown in Figure 4.4.10 and 4.4.11. In Figure 4.4.10, it can be seen from this figure that the linear extrapolations of the adsorption volume at low \(\alpha_s\) values intersect the y-axis at origin, revealing that MNi-5, 11 and 15 are all free of micropores. This is in accordance with the \(t\)-plots for calcined MCM-41 and other non-microporous silicas, which usually exhibit excellent linearity starting from the origin in the low pressure range [23, 24]. In Figure 4.4.11, the apparent upward deviation from the linearity on the \(\alpha_s\)-plots starts at the given \(\alpha_s\) values, at which the capillary condensation takes place, suggesting the mesopores are dominantly present in all three samples.

Therefore, in conclusion, mesoporous silicas with nickel content up to 11.8 still possess good mesostructures. For MNi-15, mesoporosity with broadened pore size distributions was confirmed. Through this modified DS method, large surface area with high nickel content can be achieved. Additionally, no micropores were found in all these three nickel containing mesoporous silicas.
4.4.4 Chemical states of nickel and its interaction with silica matrix

Up to now, mesostructural properties and nickel dispersion of the nickel-containing mesoporous have been investigated by Low-angle XRD, TEM and N\textsubscript{2} sorption measurements. However, the understanding of chemical nature of nickel itself incorporated into mesoporous silica frameworks is still unclear. In this section, wide-angle XRD, SEM, XPS, FTIR and TPR will be utilized to characterize the chemical states of nickel and its interaction with silica matrix.

To investigate the crystallinity nickel species in as-synthesized and calcined Ni-containing mesoporous silicas, wide-angle XRD patterns for MNi-11 and 15 were also collected and shown in Figure 4.4.12.

![Figure 4.4.12 Wide-angle XRD patterns for (1) as-synthesized MNi-11 and (2) as synthesized MNi-15. (# Al sample holder reflections)](image)

As shown in Figure 4.4.12, for both as-synthesized MNi-11 and MNi-15, a broad peak centred at about 23° can be found. This peak is assigned to the amorphous silica. One
series of small but sharp peaks are attributed to the reflections of Al sample holder used in XRD characterization. No reflections corresponding to the NiO or Ni(OH)$_2$ were observable. In the XRD pattern of as-synthesized MNi-11 and MNi-15 (especially the later), one broad and weak peak at about 35° also appear and increase with the nickel content. This can be attributed to the formation nickel silicate species. After calcination, such peak still remains and was indeed attributed to the formation of ill-crystallized nickel phyllosilicates [25].

As for the calcined samples, wide-angle XRD patterns are shown in Figure 4.4.13 (2θ in the pattern ranges from 15° to 70°).

Figure 4.4.13 Wide-angel XRD for (1) MNi-11 and (2) MNi-15 (# Al sample holder reflections and * NiO reflections).

From the wide-angle XRD patterns for MNi-11 and MNi-15, it can be seen from Figure 4.4.13 that amorphous silica support gives the expected peak centred at about 23°. Two small peaks at 38.4° and 44.9° may due to aluminum signals of sample holder. Although the peaks at about 37.3°, 43.2° and 62.9° assigned to the existence of
encapsulated bulk crystalline NiO in the sample aggregates are not so strong compared with noise signal, sporadic dispersions of bulk NiO particles of size larger than 50 nm independent of mesostructures were found in SEM photographs. As shown in Figure 4.4.14 and 4.4.15, only very scarce NiO particles can be identified over large areas in MNi-11 and MNi-15. The formation of bulk NiO can be attributed to the precipitation of Ni(II) ions in basic condition to form Ni(OH)$_2$, and then NiO after calcination.

![SEM photograph of MNi-11](image)

**Figure 4.4.14** SEM photograph of MNi-11.
Figure 4.4.15 SEM photograph of MNi-15.

Figure 4.4.16 Comparison of wide-angle XRD for 1) MNi-11-D and 2) MNi-11 (# Al sample holder and * bulk NiO reflections).
Additionally, a weak and broad peak at around 35° in Figure 4.4.13 is also visible for MNi-11 and gets stronger for MNi-15 appear. It can also be assigned to ill-crystallized nickel phyllosilicates species [25].

It is worth noting that, although there is the formation of extremely small amount of bulk NiO independent of the mesophases, the effectiveness of incorporation of nickel into the mesophases using our method is still significantly higher than those synthesized by the unmodified DS method. Wide-angle XRD pattern for MNi-11-D and MNi-11 can be compared. MNi-11-D was synthesized by the DS method with the same composition in the synthesis mixture as MNi-11. As shown in Figure 4.4.16, much stronger NiO inflections can be found for MNi-11-D compared with MNi-11. Importantly the nickel content in mesophases is much lower than that of MNi-11 as proved by the EDX results; only 4.1wt% was found to be incorporated into the mesophases. Therefore, the modification of TEOS with nickel species is the key step to incorporate higher amount of nickel species into the silica frameworks than using the unmodified DS Method.

It is believed that the connection of nickel ions with TEOS [13, 14] makes the co-hydrolysis and co-condensation occur at molecular level so that the homogeneous dispersion of the Ni in the frameworks of silica can be realized. This allows the incorporation of high amount of nickel into the silica frameworks.

From the wide-angle XRD results, ill-crystallized nickel phyllosilicates were formed. The amount of nickel phyllosilicates increased with the nickel content from 5 to 15wt%. Sporadic bulk NiO particles were found by SEM although no clear bulky NiO reflections were seen in XRD pattern. In contrast, the unmodified DS method led to formation of much more extra-framework bulk NiO and low nickel loading into mesophases. Therefore, our method can lead to the high incorporation of high amount of nickel into the mesophases with satisfactory mesostructures.
More and further information about the chemical states and interactions of nickel with silica can be found in XPS and FTIR results. XPS is widely used in catalysis because it allows the determination of the chemical state of the elements of the solid surface (oxidation number, electronic interactions with neighbouring elements).

XPS spectra of samples MNi-11, 15 are shown in Figure 4.4.17. It can be seen that the surfactants have been burned off after the calcination at 550 for 6 hours with the heating ramp of 1 per min, leaving unnoticeable carbon signals. Like most transition metals, nickel presents a relatively complex 2p XP spectrum because of the presence of a satellite (shake-up) on the high binding energy side assigned to a ligand-metal charge transfer for nickel oxide [26]. The shift between shake-up satellite and the main peak is about 6±1eV; the shift and the relative intensities depend on the nature of the ligands and on the electronic charge of the metal (i.e. the oxidation state and the interactions with the support).

![Figure 4.4.17](image_url)

Figure 4.4.17 XP spectra of MNi-11, 15.
As shown in Figure 4.4.18, in the left row, Ni 2p\(^{3/2}\) bands were fitted with three peaks very well: one band at 854.5±0.2 eV, attributed to the Ni\(^{2+}\) in Ni-O phases without or with weak interactions with silica [26-30]; one band at around 862.5 eV corresponding to the shake up satellite structure of Ni\(^{2+}\); and the primary bands at around 857.2 eV due to the formation of nickel phyllosilicates or strong interactions between the Ni-O phases and silica support. Detailed results of deconvolutions are included in Table 4.4.2.

![Figure 4.4.18](image)

**Figure 4.4.18** XP Ni 2p\(^{3/2}\) spectra (left row) and O 1s (right row) of calcined MNi-5 (top), 11 (middle), 15 (bottom).

In fact, the band at 857.2 eV can be attributed to interactions of Ni-O phases and silica support via Si-O-Ni bonds or the formation of nickel phyllosilicates, Ni\(^{2+}\) species in...
Ni(OH)$_2$, or Ni$^{3+}$ in Ni$_2$O$_3$. However, the existence of Ni(OH)$_2$ could be rejected for the reason that the calcination at 550°C for 6 hr will result in the complete transformation of Ni(OH)$_2$ to nickel oxide. Because the peak at about 867eV cannot be found, which is assigned to the shake-up satellite of Ni$^{3+}$ in non-stoichiometric black NiO, therefore the existence of Ni$^{3+}$ can be ruled out. Evidence that all synthesized samples show slight yellowish colour instead of black colour also proves the non-existence of Ni$^{3+}$. From the results of FTIR and wide-angle XRD, the presence of ill-crystallized nickel silicates was demonstrated. From the results of TPR, Ni species in these samples are much more difficult to reduce than bulk NiO because of their strong interaction with silica or formation of nickel silicates. At higher temperatures up to 700°C, there is still H$_2$ consumption. So it is more likely that nickel phyllosilicates or Ni-O phases strongly interacting with silica supports were formed.

![Binding energy (eV)](image)

**Figure 4.4.19** Deconvolution of XP Ni 2p$^{3/2}$ spectra of MNi-15 excluding the Ni 2p$^{3/2}$ peak corresponding to Ni$^{2+}$ in NiO phase.

With the increasing nickel content, the peaks at 854.3eV increase correspondingly, indicating the growth of Ni-O phase as observed in the Figure 4.4.18(left). On the one
hand, in similar Ni/SiO₂ system, the presence of the nickel oxide clusters has also been proved [24, 25, 27, 31]. Results from EXAFS showed the existence of nickel oxide clusters [24, 25]. In our case, for MNi-15, deconvolution excluding the peak at about 854.4eV, correlating with the formation of Ni-O phase, leads to bad fitting as shown in Figure 4.4.19. Especially in the circled area, the fitted line (red) deviates from the experimental line (black one). On the other hand, the influence of sporadic bulk NiO phase (see section 4.4.4, wide-angle XRD and SEM results) cannot be ruled out.

Due to the complicated existing forms of nickel in our synthesized nickel containing mesoporous silica, the Ni-O phases were simply divided into two categories: one is Ni-O phase with weak or without interaction with silica support, and the other is Ni-O phase with strong interaction with silica support or Ni-O species in nickel phyllosilicates. The relative percentages of NiO phases with weak or without interaction with silica are given in Table 4.4.2. Clearly, Ni-O phases increase slightly with increasing Ni content. However, majority of Ni is still present in nickel species with strong interaction with silica or in nickel phyllosilicates. This is also in agreement with the TPR results, no peak due to the reduction of NiO was found.

The O 1s core levels of these samples are also shown in Figure 4.4.18, right row. Results of fitting analysis show that the formation of Ni-O phase (O 1s core levels are clear resolved at 530.2eV) [29], and the interactions of Ni-O phases with silica support (O 1s at 531.6eV) as well. This is in good agreement with the above discussions.

As abovementioned, the satellite peaks corresponding to the Ni³⁺ from non-stoichiometric NiO cannot be found. Instead, the bands at 857.2eV and satellite at 862.5eV are always observed (therefore Ni²⁺ satellite splitting reaches to only 5.3eV). The satellite splitting of Ni²⁺ 2p in pure NiO is about 7.0eV and about 6.0eV for nickel silicates [32, 33]. Therefore, Ni²⁺ strongly interacting with silica support or existing in nickel silicates should be more prominent than those in Ni-O phase with weak or
without interaction with silica support. This can also be seen from Table 4.4.2, Ni\textsuperscript{2+} always constitutes the majority with regard to Ni\textsubscript{w}\textsuperscript{2+}.

### Table 4.4.2 Ni 2p\textsuperscript{3/2} binding energies (eV) for the calcined MNi-5, 11 and 15\textsuperscript{a}.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ni\textsuperscript{3+}</th>
<th>Ni\textsubscript{w}\textsuperscript{2+}</th>
<th>Ni\textsubscript{s}\textsuperscript{2+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>MNi-5</td>
<td>--</td>
<td>854.6(8)</td>
<td>857.1(92)</td>
</tr>
<tr>
<td>MNi-11</td>
<td>--</td>
<td>854.4(11)</td>
<td>857.2(89)</td>
</tr>
<tr>
<td>MNi-15</td>
<td>--</td>
<td>854.7(13)</td>
<td>857.2(87)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}: Ni\textsubscript{s} represents nickel oxide (II) with weak or without interaction with silica support; Ni\textsubscript{w}\textsuperscript{2+} strongly interacting with silica support. The relative percentages (%) of samples are given within the brackets according to the areas of deconvoluted peak.

### Table 4.4.3 Surface atomic ratios of MNi-5, 11 and 15.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Surface atom ratio (Ni/Si)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As-synthesized</td>
</tr>
<tr>
<td>MNi-5</td>
<td>0.06</td>
</tr>
<tr>
<td>MNi-11</td>
<td>0.097</td>
</tr>
<tr>
<td>MNi-15</td>
<td>0.15</td>
</tr>
</tbody>
</table>

From the atom ratio of Ni and Si, the migration of nickel species during the aging process or followed calcination can be studied. As shown in the Table 4.4.3, for every sample, the ratio of Ni to Si of calcined sample decreased in comparison with as-synthesized ones. No migration of nickel oxide from the channel to the outer surface took place. This can also be evidenced by the TEM photographs, in which no nickel oxide particles bigger than the mesopores can be seen. Not surprisingly, surface Ni/Si ratio increases from 0.05 for MNi-5 to 0.15 for MNi-15 with more nickel incorporated into the latter.

In a word, according to the XPS results, there are strong interactions between the nickel and silica supports— even the formation of nickel silicates as demonstrated by wide-angle XRD and below FTIR results. Nickel phases with strong interaction with
silica are further proved by XPS to be the predominant phases with regard to the NiO phase with weak or without interaction with silica support.

The IR technique was also employed to identify the formation of nickel silicates and silica based on the bands characteristic of constitutional hydroxyls groups.

Figure 4.4.20 The $v_{OH}$ stretching bands in FTIR spectra for four samples after pre-treatment at 673K for 2h: (1) MNi-5; (2) MNi-11; (3) MNi-15 and (4) MNi-00.

The differences of position of $v_{OH}$ bands can be used to differentiate phyllosilicates from silica. For the untreated samples (the IR spectra are not shown here), all of them present the broad peaks around at 3440 cm$^{-1}$ in the OH stretching frequency range, which is due to presence of water molecules. Such peak is weakened after pre-treatment at 673K for 2hr [34]. Figure 4.4.20 shows the $v_{OH}$ stretching bands in FTIR spectra for MNi-5, 11, 15 and mesoporous silica. It can be seen from this figure that, there is also a small peak for every nickel-containing sample at about 3647 cm$^{-1}$ due to the $v_{OH}$ stretching bands of nepouite phyllosilicates. The $v_{OH}$ bands can be
observed at 3740 cm\(^{-1}\) belonging to silica, 3622 cm\(^{-1}\) for the stretching \(\nu_{OH}\) bands of talc-like phyllosilicates. The bands at 3741 cm\(^{-1}\) exhibited by all samples can be assigned to the free OH groups on the surface of silica independent of nickel content [35]. However, as to the band at 3622 cm\(^{-1}\), getting stronger with increasing nickel containing, it suggests the presence of increasing amount of talc-like phyllosilicates [34, 36-39]. It is safe to conclude that the nepouite and the talc-like nickel phyllosilicates coexist.

Figure 4.4.21 The \(\delta_{OH}\) and SiO bands in FTIR spectra for four samples: (1) MNi-5; (2) MNi-11; (3) MNi-15; (4) MNi-00.

In the \(\delta_{OH}\) region (Figure 4.4.21), for the MNi-5, in which less nickel species were incorporated, no distinct peaks in the range from 650 cm\(^{-1}\) to 750 cm\(^{-1}\) exist. For MNi-11 provides two weak peaks around 665 cm\(^{-1}\) and 710 cm\(^{-1}\), and for the samples of MNi-11 and 15, there are two small but clear doublets at around 665 cm\(^{-1}\) and 710 cm\(^{-1}\). The 710 cm\(^{-1}\) band represents the \(\delta_{OH}\) vibration of isolated OH surrounded by three Ni atoms, whereas a slightly broad 665 cm\(^{-1}\) band has already been assigned to a
tetrahedral SiO mode: the formation of talc-like phyllosilicates [24, 25, 36, 27, 29-39]. Meanwhile, the δOH band at 710 cm\(^{-1}\) can be used to differentiate the crystallized talc phyllosilicates from the nepouite [38, 39]. However, in our case the presence of band at 710 cm\(^{-1}\) cannot rule out the existence of nepouite nickel silicate that can also give peak at about 670 cm\(^{-1}\), which is in agreement with results from bands in the OH stretching frequency range [36-39]. According to other literature, FTIR absorption bands at 660–670 cm\(^{-1}\) can be assigned to Si–O–Fe symmetric stretching [40]. Additionally, bands in the range from 520 cm\(^{-1}\) to 654 cm\(^{-1}\), which have been used as characteristic of δOH bands of nickel hydroxide [36], cannot be observed as well. Furthermore, although the Ni-O stretching vibration was overlapped by the dominant band at 463 cm\(^{-1}\) corresponding to the Si-O-Si or O-Si-O bending mode [41], the shifts from 463 cm\(^{-1}\) for the pure silica to around 469 cm\(^{-1}\) for MNi-15 due to interactions between the Ni species and silica matrix can be observed (as shown in Figure 4.4.22). Other samples showed the shifts from 463 cm\(^{-1}\) peak of pure silica: 464 cm\(^{-1}\), 466 cm\(^{-1}\) and 469 cm\(^{-1}\) for MNi-5, 11 and 15, respectively.

![Figure 4.4.22 IR spectra for samples pre-treated: (1) MNi-5; (2) MNi-11; (3) MNi-15; (4) MNi-00.](image-url)
Moreover, the peaks at about 972 cm\(^{-1}\) have been attributed to the formation of Si-O-Ni bands by others [42]. But this peak was also strongly influenced by the presence of silanol groups in calcined silica, because it is well known that stretching vibration of many Si-O- defect sites, including the Si-OH groups, can give such peak at about 970 cm\(^{-1}\) as well [43-45]. So it is clear that they cannot be used to ascertain the formation of increasing Ni-O-Si bonds in these nickel-containing mesoporous silica. However, difference spectra (shown in Figure 4.4.23) make it possible to differentiate the Si-O-Ni bonds from other Si-O defects, such as Si-OH groups. The peaks, at 700 cm\(^{-1}\) assigned to the mixtures of two kinds of nickel silicates mentioned above and those at about 1011 cm\(^{-1}\) as well as broad bands around, increase with the increasing nickel content. This supports the formation of increasing amount of Ni-O-Si bands with the increase in nickel content [36, 38].

![Figure 4.4.23](image_url)

**Figure 4.4.23** Difference spectra of (1) MNi-5 minus MNi-00; (2) MNi-11 minus MNi-00; (3) MNi-15 minus MNi-00.
In Figure 4.4.23, spectra of the pure silica was subtracted from the spectra of four nickel oxide containing samples which were multiplied by certain factors to make the asymmetric and symmetric Si-O stretching bands respectively at around 1105 and 800cm⁻¹ as close as possible. It is because the band at 1105cm⁻¹ is due to the asymmetric SiO bond of silica and the band at 800cm⁻¹ is ascribed to symmetric SiO bonds of silica support. This makes possible the examination of Ni-O-Si bonds.

Interestingly, the SiO bands characteristic of tetrahedral SiO₄ in silica at around 1105cm⁻¹ (asymmetrical stretching vibration) with a shoulder of 1230cm⁻¹ and 810cm⁻¹ (symmetrical stretching vibrations) are present. Another bending vibration at around 470cm⁻¹ can also be observed. They are analogous to those of pure silica, indicating the frameworks of silica did not change too much by the introduction of nickel species.

Therefore, the wide-XRD and SEM confirmed the formation of sporadic bulk NiO phase and nickel phyllosilicates as well. Nickel phases with strong interaction with silica are further proved by XPS to be the predominant phases with regard to the NiO phase with weak or without interaction with silica support. According to FTIR results, it can be seen that two kinds ill-crystallized nickel phyllosilicates can be distinguished. Difference FTIR spectra confirmed the presence of Si-O-Ni bonds, which could be in the nickel phyllosilicates or in the interphase between NiO phases and silica support.

Additionally, TPR was also regarded as a simple and direct technique to differentiate nickel species with regard to interactions with silica support. The weaker the interactions of the nickel species with silica matrix are, the lower the temperatures needed for the reduction are.
Figure 4.4.24 TPR curves of (1) MNi-11 and (2) bulk black NiO.

Figure 4.4.24 shows the TPR curves of MNi-11 and bulk black NiO. From this figure, it can be found that for pure bulk NiO, it can be easily reduced at temperatures lower than 370°C. However, for MNi-11, one broad peak centred at around 550°C appears and extends even to 900°C. It gives further evidence of the formation nickel phyllosilicates. According to the FTIR results, nepouite phyllosilicates coexist with small amount of tale-like phyllosilicates in MNi-11. As reported by Burattin, et al. [46], the temperature for reduction of the former is at about 600°C and the later at about 900°C. This explains the broad peak at about 550°C and still consumption of H₂ at 900°C. The TPR results give further support of the formation nickel phyllosilicates or NiO phase strongly interaction with silica support. Additionally, a distinct peak due to the reduction of bulk NiO cannot be found, which corroborate the scarcity of bulk NiO phases or NiO phase weakly interacting with silica base. This is in good agreement with the results of XRD, TEM, SEM, FTIR and XPS results.
4.4.5 Coordination studies of nickel in Ni-containing mesoporous silica

**Figure 4.4.25** UV-visible Diffuse Reflectance spectra of samples: (1) MNi-5, (2) MNi-5 calcined at 973K, (3) MNi-15 and (4) MNi-15 calcined at 973K.

**Figure 4.4.26** UV-visible Diffuse Reflectance spectra of samples: (1) MNi-5, (2) MNi-15 and (3) MNi-11-D.
Chapter 4 Ni-containing mesoporous silica systems

Diffuse-reflectance UV-vis spectroscopy is a sensitive tool that has been widely used to detect the presence of framework or extra-framework active species, for example, Zn, W, Ni, Mo and so on, which are incorporated into the mesoporous materials [47]. In our case, UV-vis DRS spectra can be used to determine the state of nickel species incorporated into the mesophases. Due to the condition employed for the synthesis of these samples (calcined at 550°C for 6 hr), the presence of Ni(OH)₂ can be ruled out. In the visible region, samples 1-4 (see Figure 4.4.25) all contain a very broad band between 600 and 900 nm with a small peak centred at around 720 nm together with a broad hump at about 770 nm. Another peak appears at around 420 nm and a small sharp peak at 384 nm. These peaks get stronger with increasing amount of nickel incorporated and can be assigned to d-d transitions of Ni²⁺ ions in octahedral or distorted octahedral coordinated environments, such as in NiO or nickel hydrosilicates [47a, 48-55]. Meanwhile, peak at 384 nm indicates the presence of bulk NiO particles [47a, 48]. It is clear from Figure 4.4.25 that calcination at 700°C did not result in significant change in the UV-vis-DRS spectra. In Figure 4.4.26, the UV-vis-DRS spectrum of MNi-11-D, which was synthesized via the unmodified DS method, was also shown. MNi-11-D was confirmed to contain much more bigger NiO particles and much less nickel within mesophases by the XRD and EDX results, while MNi-5 and MNi-15 contains most of nickel in mesophases. It can be seen from Figure 4.4.26 that peaks at 380 nm and 720 nm increase with more bulk NiO and can be attributed to the Ni²⁺ in NiO, whereas the peak at 770 nm becomes stronger from MNi-5 to MNi-15 can be assigned to Ni²⁺ ions in nickel hydrosilicates. This suggests that coexistence of nickel silicates and NiO in MNi-5 and MNi-15. The predominant peak at 770 nm and a small shoulder at 720 nm also prove the scarcity of NiO phases. Such conclusions are in good correlation with those of FTIR, XPS, and XRD.

In the Figure 4.4.25 and 4.4.26, one shoulder at about 540 nm can be found for MNi-15 and MNi-5. Such absorption has also been observed in the Ni-containing zeolites, and was attributed to tetrahedrally coordinated Ni(II) ions in the zeolites. In our case, it results from the nickel (II) ions tetrahedrally incorporated in the silica frameworks.
On the other hand, in MNi-11-D, such peak can not be found, indicating that little of nickel (II) ions was loaded into the silica walls in a tetrahedral environment [56-58].

Therefore, according to the UV-vis-DRS results, nickel in NiO and nickel phyllosilicates are six coordinated, while some Ni centres are in coordination environment of four.
4.5 Reduced Ni-containing mesoporous silica systems

4.5.1 Introduction

In section 4.4, the synthesis and characterization of nickel-containing mesoporous silica with different nickel contents have been discussed. In this section, such nickel-containing silicas were activated by reduction using H₂ at 500°C and 650°C, respectively. Various characterization techniques were employed to elucidate structural properties and chemical state of nickel after activation. After activation, MNi-5 was named after MNi-5-R500 with R means the reduction and 500 stands for the temperature at which the reduction was conducted. The rest can be deduced by analogy. Figure 4.5.1 shows the pictures of samples before and after reduction. It can be seen from this figure that the calcined samples are pale yellow, and after reduction all the samples turn greyish even black. Samples reduced at 650°C are darker than those reduced at 500°C, indicating the greater degree of reduction at 650°C.

![Figure 4.5.1](image)

**Figure 4.5.1** Colour changes of calcined samples before and after reduction at 500°C and 650°C, respectively.
4.5.2 Mesostructural ordering of reduced Ni-containing mesoporous silica

The low-angle XRD patterns for MNi-5-R500, MNi-11-R500 and MNi-15-R500 were given in Figure 4.5.2. It can be seen from this figure that the strongest (100) reflections are clearly visible for all of samples. Compared with the calcined samples, these reduced one shows similar patterns, indicating that the reduction at 500°C did not change the mesostructures much. For MNi-5-R500, analogous to M41S family, well resolved low-angle peaks show that it possess the most regular and ordered mesostructures in comparison with the other two. For MNi-15-R500, (110), (200) and (210) reflections cannot be distinguished and only a wide hump can be observed. It is also notable that the (100) reflection is quite broadened and higher-angle peaks disappear, revealing the formation of disordered mesostructures.

The $d_{100}$ of MNi-15-R500 (4.25nm) is bigger than that of MNi-11-R500 (3.81nm). Both are also larger than the $d_{100}$ of pure mesoporous silica, 3.38nm. It can be
Chapter 4 Ni-containing mesoporous silica systems
evidenced as loading more nickel into the silica frameworks of MNi-15-R500 than
MNi-11-R500. Compared with those of calcined one (see Table 4.4.41),
MNi-15-R500 (4.25nm) and MNi-11-R500 both show slight shrinkages. This further
proves the reduction to some extent of nickel species in the silica walls.

Figure 4.5.3 Low-angle XRD patterns for reduced samples at 650°C: (1)
MNi-5-R650, (2) MNi-15-R650.

In Figure 4.5.3, low angle XRD patterns for MNi-5-R650 and MNi-15-R650 are
given. It can be seen from this figure that mesostructures are still intact upon
reduction at 650°C compared with calcined MNi-5 and MNi-15. However, the \( d_{100} \)
values of MNi-5-R650 and MNi-15-R650 show further decrease to 3.62 and 4.05,
respectively. This can be explained as the greater reduction of samples at 650°C that
those at 500°C. This is in agreement with the colour changes shown in Figure 4.5.1.
It is apparent that all the samples possess stable mesostructures before and after the
reduction. Nevertheless, reduction at 650°C resulted in further decrease in the
\(d\)-spacings than at 500°C, indicating greater reduction of nickel species in the mesoporous silica walls.

### 4.5.3 Surface area and porosity of reduced Ni-containing mesoporous silica

Figure 4.5.4 shows \(N_2\) sorption data for MNi-15-R00. Inflection in the range of 0.2~0.4 can be observed, characteristic of the capillary condensation in mesopores. Figure 4.5.5 shows the pore size distributions calculated by the BJH model. As seen from Figure 4.5.5, the maximum probable distribution of mesopores of MNi-15-R500 material is at about 2.9nm in size. The observation that back-extrapolation of the \(\alpha\)-plot of MNi-15-R500 intersects the \(y\)-axis below zero (-42ml (STP)/g) can be interpreted by the pore condensation occurring at very low relative pressure \((p/p^0)\) (see Figure 4.5.6). This is not in accordance with calcined MNi-15, revealing the modification of mesostructures after reduction. High surface area of 674 m\(^2\)/g and pore volume up to 0.62cm\(^3\)/g were achieved.

![Figure 4.5.4 N\(_2\) adsorption-desorption isotherm of MNi-15-R500.](image-url)
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Figure 4.5.5 Pore size distributions of MNi-15-R500.

Figure 4.5.6 $\alpha_s$-plot analysis of MNi-15-R500.
4.5.4 Nickel chemical states of reduced Ni-containing mesoporous silica

Figure 4.5.7 shows the wide-angle XRD patterns for MNi-5, 11 and 15-R500. Besides the big hump centred at about 23° due to the amorphous silica, no reflections due to the nickel oxide can be found. A small peak at about 44.5° overlapping with Al sample holder reflections can be seen. Observation of the disappearance of small broad hump at around 35° present in calcined MNi-11 and MNi-15 can be explained as the destruction of ill-crystallized nickel silicates. However, wide-angle XRD for MNi-15-R500 (see Figure 4.5.8) after extended collection time (and using silicon support instead of Al sample holder to avoid overlapping peaks of Al with Ni⁰) shows that only weak and broad reflection at about 44.5° can be found, attesting the presence of metallic nickel. The reduction of nickel species can also be seen from the colour changes: from pale yellow for the calcined to grey after reduction as shown in Figure 4.5.1. The low signal-to-noise ratio does not allow for the calculation of particle size of Ni⁰ particles.
From Figure 4.5.9 of the wide-angle XRD pattern for MNi-15-R650, it can be seen that the stronger peaks at 44.5° than that shown in Figure 4.5.8, indicating the reduction of nickel species and growth of nickel particles. NiO reflections cannot be observed from this figure either. Peak located at about 35° due to the formation of nickel
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Phyllosilicates cannot be found either, suggesting the reduction of nickel phyllosilicates.

Figure 4.5.10 TEM photographs of (A) MNi-5-R500, (B) MNi-11-R500 and (C) MNi-15-R500. The bars are 50nm.

From the TEM shown in Figure 4.5.10, disordered mesostructures can be confirmed for MNi-15-R500, while ordered mesopores can be seen for MNi-5-R500 and MNi-11-R500. This is in accordance with results of low-angle XRD. Additionally, very small nickel (around 3nm in size) particles are visible and embedded in silica walls in MNi-11-R500 and MNi-15-R500, except in MNi-5-R500. From Figure 4.5.11, it can be found that nickel particles (around 5nm in size) exist and are dispersed evenly. This also proved the greater reduction at 650°C and excessive growth of nickel...
particles during the reduction. Clearly, the reduction conditions need to be optimised to obtain more fine nickel particles.

Figure 4.5.11 TEM photograph of MNi-15-R650.

In conclusion, wide-angle XRD pattern and TEM confirm the comparable mesostructures before and after reduction as elucidated by low-angle XRD
measurements. Intact mesostructures and greater reductions are found for samples reduced at 650°C. Very small nickel (around 3nm in size) particles are visible and embedded in silica walls in MNi-11-R500 and MNi-15-R500. Greater reduction at 650°C caused excessive growth of nickel particles. This is in accordance with the wide-angle XRD results.

Given that an average $T \cdots T$ ($T=\text{Ni or Si}$) distance of ~0.3nm, the walls between channels should, therefore, be constructed by only four tetrahedral $\text{TO}_4$ except for isolated Ni atoms which are entrapped in the walls and thus completely shielded by the silica walls and are inaccessible from channels. Therefore, in our case, it is noteworthy of noting that the accessibility of Ni clusters (>2nm) from channels can be guaranteed because of the thin walls of only about 1~2nm.

According to the XRD, TEM and $\text{N}_2$ sorption measurement, reduction at 500 and 650°C did not cause significant collapse of mesostructures. Ni$^0$ clusters of around 3nm can be obtained by reduction at 500°C, while reduction at 650°C led to growth of nickel particles to about 5nm. Nickel phyllosilicates reflections can no longer be seen in the wide-angle XRD patterns, indicating the destruction of nickel phyllosilicates. However, the chemical states of nickel in reduced Ni-containing mesoporous silica are still unknown. XPS was used to examine the changes in the chemical states of nickel due to the reduction.

Figure 4.5.12 shows the deconvolution of XP Ni 2p$^{3/2}$ spectra of MNi-5, 11 and MNi-15. From this Figure, it can be seen that the shapes of main nickel phases are quite similar to those of calcined. Only the positions of main band of Ni 2p$^{3/2}$ core level shifted from 857.4eV to 856.9eV after the reduction at 500°C. This is also observed in the case that there were strong interactions between the Ni$^{2+}$ and silica support [59]. The presence of this dominant peak shows that the nickel silicates are hard to be completely reduced at 500°C. However, the band at about 854.5±0.2eV disappeared and a new band at 852.3±0.1eV appeared, suggesting that the reduction of Ni-O phases
without or with weak interaction with silica. The estimated reduction degree is only about 5% for MNi-15-R500 (The percentages of nickel been reduced, calculated by taking into account the integrated peak area of Ni\(^0\) against the Ni\(^{2+}\) signals, including the satellite peaks). However, such estimation through this method underestimates the reduction degree. Because XPS is a surface sensitive technique, Ni\(^0\) inside the metallic crystallites and located in the inner part of sample do not contribute to the Ni\(^0\) XP signals.

Figure 4.5.12 Deconvolutions of XP Ni 2p\(^{3/2}\) spectra of MNi-5-R500 (top), MNi-11-R500 (middle) and MNi-15-R500 (bottom).
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Figure 4.5.13 Deconvolutions of XP Ni 2p$^{3/2}$ spectra of MNi-5-R650 (top one) and MNi-15-R650 (bottom one).

The XPS measurements were also conducted on the samples reduced at 650°C. As shown in Figure 4.5.13, deconvolutions of XP Ni 2p$^{3/2}$ spectra of MNi-5-R650 and MNi-15-R650 were given. It is clear that MNi-5-R650 and MNi-15-R650 appear different compared with MNi-5-R500 and MNi-15-R500. For MNi-5-R650 (Figure 4.5.13, top), the Ni 2p$^{3/2}$ band was significantly weakened, and peak corresponding to the Ni$^0$ increased, indicating the higher reduction degree at 650°C (46%) than at 500°C. As seen from the Figure 4.5.13 (bottom), peak at 854.3eV still exists and can be explained as the re-oxidation of Ni$^0$. Reduction degree for MNi-15-R650 can be
estimated up to 15%. Thus by manipulating reduction conditions high reduction degree, nickel particle size and distributions can be optimized.

4.5.5 Nickel coordination of reduced Ni-containing mesoporous silica

![UV-Vis-DRS spectra of calcined and reduced MNi-5, 15.](image)

*Figure 4.5.14 UV-Vis-DRS spectra of calcined and reduced MNi-5, 15.*

It was confirmed in section 4.4.5 that in the calcined Ni-containing mesoporous silica there are 6-coordinated nickel in NiO (720nm) and nickel phyllosilicates (770nm) and some Ni centres are in 4-coordinated environment (540nm). Figure 4.5.14 gives the
UV-Vis-DRS spectra of calcined MNi-5, 15, and reduced at 500°C and 650°C. From this Figure, it can be seen that the broad peaks centred at about 770nm were noticeably weakened after the reduction. After reduction at 500°C, MNi-15-R500 still has a weak peak left. However, Greater reduction at 650°C led to the complete disappearance of this peak. This indicates that profound changes in the coordination environments of the Ni(II) happened during the reduction. Additionally, peaks at about 380 and 720nm strengthened with the increasing reduction temperatures, revealing the re-oxidation of the reduced Ni⁰ species. This is in good accordance with the XPS results.

4.6 Conclusions

(1) A modified DS method has been developed. In this method, the connection of nickel ions with TEOS makes the co-hydrolysis and co-condensation possibly occur at molecular level so that the homogeneous dispersion of the Ni in the frameworks of silica can be realized. This allows the incorporation of high amount of nickel into the silica frameworks.

(2) According to the XRD, TEM, EDX, N₂-sorption measurements, via the modified direct synthesis method, not only can higher amount of nickel (up to 14.7wt.% Ni) be evenly incorporated into the mesophases but also mesoporous structures are still satisfactory when high amounts of nickel was incorporated. No significant micropores existed in all calcined samples. The mesoporous surface area and pore volume obtained were quite high when considering the weight increase due to the incorporation of nickel species of high density into mesoporous silica.

(3) Nickel was proved to be incorporated into the mesophases instead of formation of simple mixture of NiO and siliceous mesoporous silica. Although sporadic bulk NiO was found, but the majority of nickel species existed as nickel strongly interacting with silica, as elucidated by FTIR, XRD, UV-vis-DRS and XPS results. No Ni³⁺ was found to be present. In contrast, for a sample prepared by the unmodified direct synthesis method, nickel was mainly present as bulk NiO phases.
After reduction at 500°C, nickel clusters (around 3nm in size) were found to be embedded in the silica walls. Mesostructures were found to be intact. Reduction at 650°C caused higher reduction degree and growth of Ni^0 particles bigger than the mesopores.

References


5.1 Introduction

Mesoporous silicas, innovatively synthesized through self-assembled surfactants and inorganic species, has been a subject of much interest due to their porous structure and high surface area, ordered frameworks and narrow pore size distributions (see Chapter one, and two). However, siliceous mesoporous silica is of limited use as a catalyst due to the lack of acidic sites [1]. Therefore, many elements such as B, Al, Mn, Ti, V, Nb, Zr etc. have been incorporated into/onto the mesoporous silica to create catalytic active sites [2, 3].

TiO₂ is well known as a large bandgap semiconductor with versatile catalytic activities. For example, silica-supported titania, with improved mechanical strength, thermal stability and surface area, is active for acid-catalyzed reactions such as phenol amination [4] butene isomerization [4-6], 2-propanol dehydration [7], and 1, 2-dichloroethane decomposition [8]. Titania also has excellent photocatalytic activity for the photodegradation of 2, 4, 6-trichlorophenol [9], aromatic pollutants like benzene, mono- and di-chlorobenzene and phenol [10]. Incorporation of titania into/onto microporous and mesoporous silica has been investigated extensively [9-13]. Varying pore geometry may provide the catalyst size or shape selectivity. Highly dispersed nano-sized titania particles confined in the mesostructures can enhance its photocatalytic activity due to quantum size effects for nano-sized semiconductor particles [14, 15]. In particular, such titania modified silica takes advantage of titania and mesoporous silica (high surface area, high thermal stability), making it more active, stable and easier to recover.

In such materials, maintenance of mesoporous surface area is of key importance because it is the mesopores that facilitate the flow of reactants into and product molecules out of the pore system. One of most extensively used method to load titania on SBA-15 is the impregnation method. However, in this method, loading high amount of titania at a time into the mesochannels (called one step impregnation method,
designated as OSI method), often leads to the blockage of mesopores due to the formation of big titania particles. For example, 10 wt.% of titania loaded on MCM-41 also cause the blockage of mesopore [16]. Less than 12wt.% of titania loading led to the loss of almost half of BET surface area of mesoporous silica [17]. 40% of pore volume was lost when 25wt.% titania are incorporated into MCM-41 [18].

Among the mesoporous silicas that are suitable as titania support, SBA-15, synthesized in 1998 by Zhao et al. [19-21], is currently one of the most prominent kinds of mesoporous silica due to its easy synthesis, good thermal stability, and high surface area. SBA-15 has been proved to be superior as a catalyst support to siliceous MCM-41 and other silica supports [22-23]. Importantly, properly synthesized SBA-15 possesses quite a number of micropores [24-29], which is due to the interaction between micelles of Pluronic surfactant (in our case is P123, PEo20PPO70PEo20) through ethylene oxide headgroups. The SBA-15 has the micropores with the pore sizes range from 1-3nm, micropore volumes range from 0.06-0.12cm³/g [24, 25], and probably present connectivity between the mesopores [24].

In the present work, micropores in SBA-15 were used to accommodate titania small particles aiming at not losing mesopore surface area or retaining the majority of mesoporous surface area upon titania grafting. This is because that high surface area and accessible mesochannels for the flow of reactant and product molecules in and out of the pore are very important for such family of materials as catalyst supports. In this project, a multistep impregnation method was developed by us. The results obtained show that the titania species can be highly dispersed on SBA-15 silica with mesostructures retained. No blockage of mesopores was acknowledged upon high loading up to 24.4wt.% (Si/Ti≈4).

Photocatalytic activities were also examined for the photo-degradation of phenol, salicylic acid in water and oestrogen in water/ethanol mixture.
5.2 Experimental

5.2.1 Materials

Titanium isopropoxide (TTIP), mesitylene (TMB), tetrachloro ethereal orthosilicate (TEOS), hydrogen chloride (37%), iso-propanol, salicylic acid, phenol, oestrogen (17β-oestradiol) and Pluronic PEO$_{20}$-PPO$_{70}$-PEO$_{20}$ (P-123 with Fw=5750) were bought from Aldrich and were used as received without further purification. The followings are the chemical structure of pluronic P123 and oestrogen.

$$\text{CH}_3 \text{HO-}(\text{CH}_2\text{CH}_2\text{O})_x\text{-(CH}_2\text{CHO})_y\text{-(CH}_2\text{CH}_2\text{O})_x\text{H}$$

PEO$_{20}$ PPO$_{70}$ PEO$_{20}$

17β-oestradiol

5.2.2 Synthesis

5.2.2.1 Synthesis of siliceous SBA-15

SBA-15 was synthesized according to the method described by Zhao et al [16, 17] with slight modification. Typically, 4g P123 was dissolved in 130g deionised water, the formed solution was kept stirring at 40°C until clear. 20ml HCl (37%) was added before TEOS was dropped in. The reaction mixture was stirred moderately for 24 hours, followed by aging at 95°C for another day without stirring. The white product was collected by filtration, and then dried at 50°C, calcined at 550°C for 6h with the heating ramp of 1°C per min. SBA-15 was then pre-treated: re-hydrated in boiling water for 2h.
Obtained hydrated SBA-15 was dried at 120°C (designated as S15-A-0) and heated at 300°C (designated as S15-B-0) for 6h.

5.2.2.2 Loading titania into siliceous SBA-15

Titania-containing SBA-15s were synthesized by impregnation method: 1.0g S15-A-0 or S15-B-0 was impregnated with 0.5g TTIP in 50g iso-propanol under vigorous stirring for 20hr at room temperature. Obtained products were separated by centrifugation, washed using iso-propanol, dried in vacuum for 40mins at 150°C and then calcined at 400°C for 4 hours. This loading procedure was repeated more than once to pickup more titania. Obtained samples are designated as S15-A-I or S15-B-i, ‘i’ means the number of loading cycle via impregnation. For convenience, S15-0 in our study refers to S15-B-0. S15-A-0 and S15-B-0 show almost no difference according to low-angle XRD results. For comparison, S15-D-1 was also synthesized using one-step impregnation method: 0.25g S15-A-0 was impregnated with 0.5g TTIP in 20g iso-propanol under vigorous stirring for 20hr at room temperature. The mixture was heated to reflux for 20hr. After boiling off the iso-propanol, obtained products were recovered and calcined at 400°C for 4 hr.

5.2.3 Photo-activity test

a) Photo-degradation of salicylic acid in water

50mg catalyst was added into 100ml solution of salicylic acid in water with concentration of 10⁻⁴mol/L. This suspension was further dispersed by ultrasound in ultrasound clean bath for 1-2mins. 8w UV lamp (Lamps UV, 8W, EL series (Fisher), working at 254nm) was used as irradiation source. During the irradiation, magnetic stirring was employed. At given intervals of illumination (2h, in our case), a specimen (5ml) of the suspension was collected using a 10ml syringe and filtered with syringe filter (Sartorius, Minispart SRP 15,pore size is 0.25μm). All the filtrates were analyzed by UV-vis spectroscopy using a Perkin-Elmer Lamda 2 Spectrophotometer. Distilled water was used as blank. The concentration of salicylic acid was determined at 296nm.
b) Photo-degradation of phenol in water
50mg catalyst was added into 100ml solution of phenol in water with concentration of 9.5×10^{-5} \text{ mol/L}. And then, steps are the same as those for salicylic acid. After acidification to pH~2.8 using 2 drops of 0.25mol/L HCl, the concentration of p-benzoquinone and hydroquinol were monitored from the UV peak at 244nm and 295nm, respectively (distilled water acidified to pH~2.8 was used as blank). And then, the concentration of phenol was determined at 287.5nm after basification to 12.3 using 1 drop of 10mol/L NaOH solution (distilled water basified to pH~12.3 was used as blank).

c) Photo-degradation of oestrogen in water/ethanol (1:1, v/v) mixture
50mg catalyst (10mg for Bulk titania) was added into 100ml water/ethanol (1:1, v/v) mixture. This suspension was further dispersed by ultrasound in ultrasound clean bath for 2mins. 8w UV lamp (Lamps UV, 8W, EL series (Fisher), working at 254nm) was used as irradiation source. At given intervals of illumination (2h), specimens (5ml) of the suspension were collected using a 10ml syringe and filtered with syringe filter (Sartorius, Minispart SRP 15, pore size is 0.25μm) and then centrifuged at 4000rpm for 10min. All the filtrates were analyzed by UV-vis spectroscopy using a Perkin-Elmer Lamda 2 Spectrophotometer. Water/ethanol (1:1 v/v) was used as blank. The concentration of oestrogen was determined at 280.6nm. Specific reaction rate was normalized by the amount of titania.

5.2.4 Characterization
The surface area measurement was carried out through BET method using adsorption data over the relative pressure range of 0.05~0.16 [30]. The pore size distributions were calculated using BJH method [31] with corrected Kelvin function: statistical film thickness (t) was calculated by Halsey equation [32]. \( \beta_r \)-plots analysis was carried out instead of using \( \alpha_s \) plot: the volume of N\(_2\) absorbed was plotted against \( \beta_r=[\ln(0.4)/\ln(p/p^0)]^{(1/2.7)} \), which should be equivalent to \( \alpha_s \) for a hypothetical nonporous adsorbent that undergoes adsorption according to Frenkel-Halsey-Hill.
Since this relationship is valid over a wide range of relative pressures, 0.003–0.994, the substitution of \( \beta_s \) for \( \alpha_s \) should be valid over the range of pressures examined by us. The calculations of \( V_{\text{meso}} \) (mesoporous volume), \( V_{\text{mi}} \), \( A_{\text{meso}} \) (mesopore volume and surface area, respectively) were carried out.

XPS studies were performed on an Escalab MKII 200R spectrometer equipped with a hemispherical electron analyzer and an Al-K\( \alpha \) X-ray exciting source (1486.6eV, 8kV, 20 mA). Binding energies (BE) were referenced to Si\( 2p \) at 103.4eV. The powders are degassed at room temperature for 3 hours before mounting on the sample hold. Samples recorded with take-off angle of 30 degrees, were pressed into pellets with smooth surface in advance of testing. The binding energy and atomic concentrations of the catalysts were calculated from the XPS results using the total integrated peak areas of Ti\( 2p \), Si\( 2p \) and O\( 1s \) regions. The spectra were smoothed, and nonlinear Shirley-type background was subtracted. Deconvolutions were carried out using the theoretical XPS bands—20% Lorenz and 80% Gauss, via a least squares algorithm. The XPS peak fitting software of XPSPEAK4.1 was used.

Raman spectra were collected with the 632.8nm line of HeNe laser (20mW) on LabRAM. Accumulation time and numbers are 5 seconds and 4 times, respectively.

Diffuse reflectance UV-vis spectra were collected on Perkin Elmer UV/Vis spectrometer (Lambda Bio 40) in the range from 250nm to 600nm with a resolution of 1nm. Reflectance data were converted to \( f(R_{\infty}) \) values using the Kubelka-Munk equation.

5.3 Multistep impregnation method

In Section 5.1, it was pointed that, to load the titania into the mesoporous silica, one-step impregnation method (OSI method) often leads to the formation of bigger guest particles in the mesochannels, which may block the exchange of reactants and product molecules in the catalysis. This method is schematically represented in Figure
5.3.1B. It can be seen from this figure that irregular bigger titania particles block or partly block the mesopores.

![Diagram of loading titania into SBA-15](image)

**Figure 5.3.1** Schematic representation of loading titania into SBA-15. The grey parts represent the silica support and the black ones represent titania phases.

However, here, a new multistep impregnation method (MSI method, as shown in 5.3.1A) will be introduced, in which there are two main characteristics:

(I) The self-limiting reaction of titanium tetraisopropoxide (TTIP) with surface hydroxyls in each loading cycle completely. In each step, the surface hydroxyls join the reaction with TTIP molecules resulting in the high dispersion of titania in mesoporous silica.

(II) Removal of residue TTIP molecules to minimise the growth of titania phase (key point), because the residue of TTIP will decompose during the calcination. In the MSI method, such residue TTIP molecules are pumped off leaving the growth of titania restricted.

In this part, two series of titania-containing mesoporous silica were synthesized.
Chapter 5 Titania-containing mesoporous silica systems

Specifically, details for the synthesis are listed in Table 5.3.1. As introduced above, titania can be immobilized on the surface of SBA-15 via the reaction of TTIP with surface hydroxyls. Therefore, the amount of titania that can pick up by silica support depends on the total accessible surface area and the surface hydroxyl density. Here, two kinds of mesoporous SBA-15 have been used to synthesize titania-containing SBA-15. Final products are designated as S15-A-i and S15-B-i, with A and B standing for the two series of silica used (A for SBA-15 pre-treated at 120°C for 6h, and B for 300°C for 6h in open air); i represents loading cycles.

Table 5.3.1 the two procedures employed to synthesize titania-containing SBA-15^a.

<table>
<thead>
<tr>
<th>Starting SBA-15</th>
<th>Pre-treatments</th>
<th>Total loading Cycles</th>
<th>Calcination</th>
</tr>
</thead>
<tbody>
<tr>
<td>S15-A-1</td>
<td>Heating the SBA-15 in the air at 120°C for 6hr</td>
<td>1</td>
<td>At 400°C 4hr in air</td>
</tr>
<tr>
<td>S15-A-2</td>
<td>Heating the SBA-15 in the air at 120°C for 6hr</td>
<td>2</td>
<td>At 400°C 4hr in air</td>
</tr>
<tr>
<td>S15-B-2</td>
<td>Heating the SBA-15 in the air at 300°C for 6hr</td>
<td>2</td>
<td>At 400°C 4hr in air</td>
</tr>
<tr>
<td>S15-B-3</td>
<td>Heating the SBA-15 in the air at 300°C for 6hr</td>
<td>3</td>
<td>At 400°C 4hr in air</td>
</tr>
<tr>
<td>S15-C-2^b</td>
<td>Heating the SBA-15 in the air at 300°C for 6hr</td>
<td>2</td>
<td>At 400°C 4hr in air</td>
</tr>
<tr>
<td>S15-D-1^c</td>
<td>Heating the SBA-15 in the air at 120°C for 6hr</td>
<td>1</td>
<td>At 400°C 4hr in air</td>
</tr>
</tbody>
</table>

^a: the loading steps and the experiment conditions are: white SBA-15 powders after pre-treatment was transferred into the iso-propanol, to which appropriate amount of TTIP was added with constant Silica: TTIP: iso-propanol weight ratio of 2: 1: 100; All the samples were pre-treated to remove the residue TTIP before heat treatment at elevated temperatures; b: the starting SBA-15 was synthesized at pH=1.0. Such SBA-15 displays slightly small BET surface area; c: weight ratio of SBA-15: TTIP: iso-propanol is 1:2:80. After impregnation with TTIP, the residue reactant was not removed. So the much of TTIP will be left, which will evaporate or decompose at elevated temperatures in the calcination and be responsible for the significant growth of titania particles.
For comparison, S15-D-1 using OSI method was also synthesized. In order to confirm the efficiency of our MSI method, all titania-containing mesoporous silica systems, which will be discussed in the following sections, were examined using varieties of characterisation techniques.

5.4 Titania-containing mesoporous silica systems

5.4.1 Mesostructural ordering of TiO$_2$-containing SBA-15

Powder X-ray diffraction (XRD) measurements were used for crystal phase identification and estimation of crystallite sizes and also extensively used to characterize the mesostructures exists in mesoporous materials. XRD pattern at low angles were recorded. The results are shown in Table 5.4.1 and Figure 5.4.1 and 5.4.2.

**Table 5.4.1 Structural parameters for siliceous SBA-15 and TiO$_2$-containing SBA-15.**

<table>
<thead>
<tr>
<th>samples</th>
<th>Titania (wt.%</th>
<th>$D_{\text{spacing}}$(nm)$^b$</th>
<th>Unit cell(nm)$^c$</th>
<th>Pore sizes(nm)$^d$</th>
<th>Wall thickness(nm)$^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S15-0</td>
<td>0</td>
<td>8.66</td>
<td>10.00</td>
<td>7.25</td>
<td>2.75</td>
</tr>
<tr>
<td>S15-A-3</td>
<td>24.4</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>S15-B-1</td>
<td>5.8</td>
<td>9.71</td>
<td>11.21</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>S15-B-2</td>
<td>7.5</td>
<td>9.71</td>
<td>11.21</td>
<td>7.73</td>
<td>3.48</td>
</tr>
<tr>
<td>S15-B-3</td>
<td>17.1</td>
<td>9.60</td>
<td>11.09</td>
<td>7.36</td>
<td>3.73</td>
</tr>
</tbody>
</table>

a: obtained by EDX equipped with TEM; b: d-spacings are calculated using the Bragg's equation; c: the unit cell parameter is $2/\sqrt{3}$ for hexagonal structure; d: the pore size are most probable pore size distributions obtained by BJH model; e: subtraction of pore sizes from the unit cell.
According to the low-angle XRD results, the existence of well-ordered mesopores over long range of silica or maintenance of the mesostructures after introduction of titania...
can be known. As shown in Figure 5.4.1 and 5.4.2, the mesoporous silica and mesoporous titania-containing silica all possess similar mesoporous structure as reported [19-21]. All the samples displayed at least three reflections: (100), (110) and (200), characteristic of hexagonal array of mesochannels. Well-resolved and sharp low-angle peaks show that the long-range ordering of SBA-15-type mesostructures remain. However, in Ti-substituted mesoporous silica [4-9], low-angle peaks weakened and became unresolved or even disappeared. This can be attributed to the poorer ordering or even collapse of mesostructures when such hetero-atoms are introduced. Such phenomena are not observed in both S15-A series and S15-B series, revealing the retention of the mesostructures upon loading titania.

Additionally, the shifts of the main peak to lower angles after grafting titania indicate that some changes in the mesostructures occurred. Usually, for un-calcined mesoporous silica, contraction upon calcination takes place due to the further condensation of hydroxyls in/on the walls. However, it did not happen to our samples, because the SBA-15, which was used as starting silica base, was calcined at 823K for 6h with a slow heating ramp of 1K per min from the room temperature, leaving little room for further condensation. Especially, it is clear that there is expanding effect, for example, the $d_{100}$ increased from 8.66nm to 9.6nm for S15-B-3 (see Table 5.4.1 and in Figure 5.4.1), and the corresponding wall thickness also went up from 2.75nm to 3.73nm. In Figure 5.4.2, the $d_{100}$ increases from 8.66nm to 9.01nm for S15-A-2. The wall thickness for S15-A-2 increases to 3.16nm from 2.75 for S15-0. This can only be explained as the inclusion of titania species into the walls leading to the expansion in walls. For the similar titania-containing mesoporous silica, unit cell enlargements were also found [10-12].

Random clogging of the mesochannels generated by aggregates of titania may cause deterioration of mesochannels ordering. Therefore, via MSI method, titania species should be dispersed in homogeneous form instead of as bigger aggregates obliteratoring
mesostructures in both series. TEM gives further evidences of the intactness of mesostructures.

Figure 5.4.3 TEM photograph of S15-B-1.
Figure 5.4.4 TEM photographs of S15-B-2.
Figure 5.4.5 TEM photographs of S15-B-3.
Figure 5.4.6 TEM photograph of S15-A-1.
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Figure 5.4.7 TEM photographs of S15-A-2.

Figures 5.4.3, 5.4.4 and 5.4.5 show the TEM photographs of S15-B-1, 2 and 3, respectively. It can be seen that hexagonally packed mesopores are visible clearly.
There are no visible titania particles in the mesopores and on the outer surfaces irrespective of the numbers of coating cycles. For A series, as shown in Figure 5.4.6 and 5.4.7, hexagonal structures are still there and no bulk titania particles visible. This indicates that mesostructures did not collapse upon loading titania via this MSI method and the dispersions of titania in both series should be high. This is in good agreement with the low-angle XRD results. These conclusions are also correlated with those by Grieken et al. [22-23], who concluded that SBA-15 is more suitable than MCM-41 to serve as titania support due to its high stability.

5.4.2 Crystallinity and size of titania clusters

After loading titania through the MSI method, the mesostructures of S15-0 are still intact, which was confirmed by the low-angle XRD and TEM results. Although no bulk titania particles were found, it is still impossible to rule out the formation of small titania clusters. Wide-angle XRD and Raman were used in this project to examine the crystallinity of titania incorporated.

![Wide-angle XRD patterns](image)

**Figure 5.4.8** Wide-angle XRD patterns for (1) S15-0, (2) S15-B-1, (3) S15-B-2 and (4) S15-B-3.
Well-crystallized anatase titania can be formed from the amorphous titania by calcination at elevated temperatures [33]. All the samples synthesized, were calcined at 400° or 500° for 4 or more hours. Amorphous titania should be transformed into crystalline one in such conditions. However, no peaks corresponding to crystalline titania in the Figure 5.4.8 and 5.4.9 can be identified, except one broad peak at about 23° corresponding to the amorphous silica base. This indicates that the titania clusters should be very small (less than ~3nm) so that they can escape from the X-ray detection.

Compared with the XRD, Raman was found to be very sensitive to crystalline anatase (see section 3.5). Raman spectra were further employed to study the crystallinity of titania. For comparison, Raman spectra of pure anatase and siliceous S15-0 were also collected and are shown in Figure 5.4.10 and 5.4.11, respectively.
Figure 5.4.10 Raman spectra of pure anatase titania.

From Figure 5.4.10, one strong peak at 144 cm\(^{-1}\) and another triplet peak at respectively at 395, 515, and 639 cm\(^{-1}\), characteristic of crystalline anatase TiO\(_2\) can be observed [34]. Additionally, small peaks at 198, 397, 923, 987 cm\(^{-1}\) are also visible in the enlargement Raman spectra in this figure. For S15-0, featureless Raman spectra
(Figure 5.4.11) only show one peak at 485 cm\(^{-1}\) assigned to the fourfold siloxane rings [35, 36]. Compared with Figure 5.4.10 and Figure 5.4.11, appearance of above triplet can be used to mark the existence or non-existence of anatase TiO\(_2\), because the strongest peak at 144 cm\(^{-1}\) due to the anatase TiO\(_2\) and peak at 137 cm\(^{-1}\) of silica overlaps.

![Figure 5.4.12 Raman spectra of S15-B-1 (bottom), 2 (middle) and 3 (Top).](image)

For S15-B series, as shown in Figure 5.4.12, anatase TiO\(_2\) exists in S15-B-3 and S15-B-2. With increasing amount of titania picked up, the triplet peaks increase. No such peaks appear in S15-B-1. Raman was found to be sensitive to crystalline anatase,
whereas amorphous titania oxide, which have wide distribution of bond angles, lead to broadened peaks. Therefore, in S15-B-3, the triplet peaks seem to be broadened, indicating that the anatase-like titania clusters, although present, are quite small.

![Raman spectra](image)

**Figure 5.4.13** Raman spectra of S15-A-1 (bottom), 2 (middle) and 3 (Top).

For S15-A series, crystalline anatase TiO₂ were not as distinct as S15-B series, as shown in Figure 5.4.13. For the sample S15-A-3, which contains the highest amount of titania, the triplets are still not as strong as those found in S15-B-3. This can be assigned to the higher dispersion of titania in S15-A series.
Therefore, according to the Raman spectra of two series of titania-containing mesoporous silica, no bulk titania phase were found, revealing titania (up to 24.4 wt.%) could be highly dispersed into/onto mesostructures through the MSI method.

Ultraviolet spectroscopy has been utilized to characterize the bulk structure of crystalline and amorphous titania-silicas [39]. Titania is a semiconductor oxide with an easily measured optical bandgap. The UV absorption threshold is a strong function of titania cluster size for diameters less than 5 nm, which can be attributed to the well known quantum size effect for semiconductors [40, 41]. Figure 5.4.14 shows the diffuse reflectance UV-vis spectra (corrected by using Kubelka-Munk equation) of S15-B-1, 2, 3, pure silica and anatase titania with particle size of about 25 nm. S15-B-2 and S15-B-3 both exhibit a band edge of less than 340 nm (big blue shifts from the band edge of bulk anatase titania at 375 nm [42-44]), revealing there are no bulk titania particles present (in fact, should be less than 5 nm in diameter), in good agreement with XRD and Raman results. Because of the limits of the instrument, the peak located lower than 250 nm cannot be observed. One peak centred at 265 nm for S15-B-3 probably attributes partially polymerized hexa-coordinated Ti species, suggesting the presence of small titania clusters (see below discussion) [45]. A small shoulder at about 265 nm for S15-B-2 can also be identified. In fact, the influence of water on the coordination of Ti(IV) species can be ruled out because this peak was still observed after 400°C treatment for 2 hours. The linkages of Ti-O-Ti in nano-domains of titania do exist.
Figure 5.4.14 Diffuse reflectance UV-vis spectra of (1) S15-B-1, (2) S15-B-2, (3) S15-B-3, and (4) S15-0.

Figure 5.4.15 Diffuse reflectance UV-vis spectra of (1) S15-A-1, (2) S15-A-2, (3) S15-A-3, and (4) S15-0.
Figure 5.4.16 Plots of \((F(R_p) \times h\nu)^{1/2}\) against photo energy of (1) S15-A-1, (2) S15-A-2, (3) S15-A-3, and (4) bulk titania.

Figure 5.4.17 Plots of \((F(R_p) \times h\nu)^{1/2}\) against photo energy of (1) S15-B-1, (2) S15-B-2, (3) S15-B-3, and (4) bulk titania.
Table 5.4.2 Results of UV-vis DRS measurements.

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Adsorption edge (nm)</td>
<td>321</td>
<td>328</td>
<td>337</td>
<td>322</td>
<td>326</td>
<td>333</td>
<td>371</td>
</tr>
<tr>
<td>Bandgap shift (nm)a</td>
<td>54</td>
<td>47</td>
<td>38</td>
<td>53</td>
<td>49</td>
<td>42</td>
<td>4</td>
</tr>
<tr>
<td>Band gap energy (eV)b</td>
<td>3.87</td>
<td>3.78</td>
<td>3.68</td>
<td>3.85</td>
<td>3.81</td>
<td>3.73</td>
<td>3.35</td>
</tr>
<tr>
<td>TiO₂ clusters size range (nm)</td>
<td>1.0-1.3</td>
<td>1.1-1.4</td>
<td>1.2-1.5</td>
<td>1.0-1.3</td>
<td>1.0-1.3</td>
<td>1.1-1.4</td>
<td>3.4-4.7</td>
</tr>
</tbody>
</table>

a: bandgap shifts are compared with the pure titania (375nm). b: the band-gap energy was calculated by the equation: $E_g (eV) = \frac{1241}{\lambda_g (nm)}$, where, $E_g$ is band-gap energy, $\lambda_g$ is the threshold wavelength.

For S15-A-1, 2, 3, similar conclusions can be drawn: the absorption edges are about 50nm shifts from those of pure titania [43, 44], suggesting the non-existence of bulk titania phases. As shown in Figure 5.4.15, a shoulder at 265nm for S15-A-2 and a peak instead for S15-A-3 can clearly be seen, which can be attributed to the formation of TiO₂ nano-domains.

The band gap energy ($E_g$) for allowed transitions was determined by finding the intercept of the straight line in the low-energy rise of $[F(R_\infty)h\nu]^1/2$ against $h\nu$ (near the absorption edge. The absorption coefficient, $\alpha$ is proportion to $[F(R_\infty)h\nu]^1/2$), where $F(R_\infty)$ is Kubelka-Munk function and $h\nu$ is the incident photon energy [46, 47]. The absorption edge, band-gap energies are given in Table 5.4.2. In the titania-containing silicas, especially titania-silica mixed oxides, such as TS-1 (with ca. 2.4 at% Ti or less), all the Ti sites are isolated tetrahedral [TiO₄] units [48-51]. The UV absorption edge of TS-1 appears at about 295nm, and absorption edge of bulk titania is at 375nm. In our case, all absorption edges for our sample are in between the values of TS-1 and bulk titania. It is known that the UV absorption threshold is a function of titania cluster size less than 5nm. As shown in Figure 5.4.16 and 5.4.17 and Table 5.4.2, the absorption edge shift decreases when titania loading increases. For S15-A-1 and
S15-B-1, the shifts from that of bulk anatase are 54nm and 53nm, respectively, drop down to 38nm for S15-A-3 and 42nm for S15-B-3. This can be attributed to the growth of titania nano-domains.

The blue shift, or increased bandgap energy, can be used to estimate the size of titania particles [41]:

\[
\Delta E_g = \left( \frac{\hbar^2 \pi^2}{2 \mu R^2} \right) \left( \frac{1.8 e^2}{\varepsilon R} \right)
\]

where \( \mu \) is the reduced effective mass \( \left( \frac{1}{\mu} = \frac{1}{m_\text{e}} + \frac{1}{m_\text{h}} \right) \) of the electron and hole, \( R \) is the particle radius, \( e \) is the elementary charge, and \( \varepsilon \) is the dielectric constant of the semiconductor [41]. Values in the ranges, 0.01-3\( m_\text{e} \), 5-30\( m_\text{e} \), and 14-184 have been reported for the effective mass of the hole, effective mass of the electron, and dielectric constant of titania, respectively [41, 52]. Kormann's values for the effective reduced masses \( m^*_\text{e}=9m_\text{e} \) and \( m^*_\text{h}=3m_\text{e} \) were used in the determination of the particle size in the present study [41]. By using the entire range of dielectric constants, corresponding titania particle sizes range was estimated and the results are listed in Table 5.4.2. The bandgap energy value for pure bulk anatase is 3.3 eV [43, 44]. Therefore, the small titania clusters with the particles size of about 1nm may only consist of about 30 TiO_2 units. Compared with both series of samples, it is clear that the particle size estimated for S15-B-3 is larger than that of S15-A-2, even though the former possesses higher titania content. It is logical that the higher OH density for the A series, which was just dried at 120°C for 6hr, whereas the starting silica for B series were calcined at 300°C for 6 hr. This led to the higher dispersion of titania species for A series. This is in good agreement with the results of Raman measurements.

In conclusion, UV-vis DRS spectra further confirm the Raman results that no bulk titania phases were formed except very small titania clusters. Moreover, according to the UV-vis-DRS results, titania cluster size can be estimated up to 1.3nm in S15-B-3.
5.4.3 Surface area and porosity of TiO$_2$-containing SBA-15

So far, the low-angle XRD and TEM measurements have shown the ordering and quality of mesostructures after titania loading via the MSI method. Especially, the Raman and UV-vis-DRS measurements further confirm the present of titania clusters (up to 1.3nm). However, surface area and porosity of such mesoporous materials are still unknown. Therefore, N$_2$ sorption measurements were carried out to characterise the textural properties of titania-containing SBA-15.

a) Physisorption of siliceous S15-0

Figure 5.4.18 N$_2$ isotherm of S15-0.

Figure 5.4.18 shows the N$_2$ isotherm of S15-0. Clear type IV nitrogen physico-sorption curve, characteristic of unique capillary condensation due to the mesoporous structure, can be seen. A sharp inflection occurs at a relative pressure in the range of 0.7~0.75, centered at about 0.72, indicating the comparable mesopore sizes compared with SBA-15 [19]. Due to the lack of desorption data on the hysteresis loops, it is
impossible to further classify the isotherms. However, according to reports of Zhao et al. [19-21], a hysteresis loop may be present in such material. The BET surface area result shows that such mesoporous silica possesses high surface area up to 792 m²/g and large pore volume, 0.95 cm³/g. Pore distribution calculation was based upon the BJH model as shown in Figure 5.4.19. It can be seen that the pore size distribution is narrow. The most probable distributed pore size was used as the mean diameter of the mesopores. For S15-0, it is about 7.25 nm.

Figure 5.4.19 Pore size distributions of S15-0 calculated by BJH model.
The $\beta_s$ plot analysis method was introduced in Chapter 3. Therefore, from Figure 5.4.20, it is easy to know:

\[ A_{\text{meso}} = (219.3-10.25) \times 2.57 = 537 \text{m}^2/\text{g} \]
\[ V_{\text{meso}} = (567.4-45.4) \times 0.001547 = 0.81 \text{cm}^3/\text{g} \]
\[ D_{\text{meso}} = 4V_{\text{meso}}/A_{\text{meso}} = 6.0 \text{nm}. \]

As pointed out in Chapter 3, $D_{\text{meso}}$ was actually underestimated. The more accurate value is about 7.0nm.

b) Physisorption of titania-containing SBA-15

Two series of titania-containing SBA-15 were synthesized. As shown in the Figure 5.4.21 and Table 5.4.3, the shape of N2 adsorption isotherms of S15-A-1 (10.2 wt. % of titania) and S15-A-2 (with 14.1 wt. % of titania) show no significant difference compared with that of siliceous S15-0. The steep inflection occurs at relative pressure in the same range of 0.70–0.75, centred at about 0.72, indicating the preservation of
mesostructures. Therefore, the changes in mesopore sizes due to the incorporation of TiO$_2$ should be small. However, the first inflection points or knees of these isotherms reveal the changes in the amount of N$_2$ adsorbed when the monolayer coverage was achieved. With increasing amount of titania loading, the amount of N$_2$ needed to reach a monolayer adsorption decreases continuously. This can be reflected with the decrease in the BET surface area, which will be discussed in detail below. Difference in relative pressures, at which sharp inflections take place, between the S15-B-2 and S15-B-3, is also tiny. Clearly, the pre-treatment of the mesoporous SBA-15 and subsequent filling of titania did not cause the collapse of mesopores or significant shrinkage in mesopore sizes. This is in good agreement with above low-angle XRD and TEM results.

<table>
<thead>
<tr>
<th>Samples</th>
<th>TiO$_2$ (wt.%)</th>
<th>S.S.A ($m^2/g$)</th>
<th>$V_{pore}^a$ (ml/g)</th>
<th>$D_{BET}$ (nm)</th>
<th>$D_{Spacing}$ (nm)</th>
<th>Wall thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S15-0</td>
<td>0</td>
<td>793</td>
<td>0.95</td>
<td>7.25</td>
<td>8.66</td>
<td>2.75</td>
</tr>
<tr>
<td>S15-A-1</td>
<td>10.2</td>
<td>724(712)$^b$</td>
<td>0.87(0.85)</td>
<td>7.67</td>
<td>9.40</td>
<td>3.18</td>
</tr>
<tr>
<td>S15-A-2</td>
<td>14.1</td>
<td>612(681)</td>
<td>0.81(0.82)</td>
<td>7.25</td>
<td>9.01</td>
<td>3.15</td>
</tr>
<tr>
<td>S15-B-1</td>
<td>5.8</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>S15-B-2</td>
<td>7.5</td>
<td>658(734)</td>
<td>0.80(0.88)</td>
<td>7.73</td>
<td>9.71</td>
<td>3.42</td>
</tr>
<tr>
<td>S15-B-3</td>
<td>17.1</td>
<td>547(657)</td>
<td>0.72(0.79)</td>
<td>7.36</td>
<td>9.60</td>
<td>3.73</td>
</tr>
</tbody>
</table>

$^a$ $V_{pore}$ was obtained at $p/p_0=0.9814$; $^b$ the values in brackets are theoretical ones calculated taking the titania weight into consideration, $Value_{theo}=Value_{exp}/(1-TiO_2\ wt.\%)$.  

Table 5.4.3 Structural parameters of S15-0 and titania-containing SBA-15.
Table 5.4.4 Results of β\textsubscript{s}-plots analysis

<table>
<thead>
<tr>
<th>Samples</th>
<th>(A\textsubscript{meso}) (m\textsuperscript{2}/g)</th>
<th>(A\textsubscript{micro}) (m\textsuperscript{2}/g)</th>
<th>(V\textsubscript{micro}) (^\text{a}) (ml/g)</th>
<th>(V\textsubscript{meso}) (^\text{a}) (ml/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S15-0</td>
<td>537</td>
<td>256</td>
<td>0.070</td>
<td>0.81</td>
</tr>
<tr>
<td>S15-A-1</td>
<td>495(482)(^b)</td>
<td>229</td>
<td>0.064(0.063)</td>
<td>0.74(0.73)</td>
</tr>
<tr>
<td>S15-A-2</td>
<td>486(461)</td>
<td>126</td>
<td>0.012(0.06)</td>
<td>0.71(0.70)</td>
</tr>
<tr>
<td>S15-B-2</td>
<td>463(497)</td>
<td>195</td>
<td>0.055(0.065)</td>
<td>0.71(0.75)</td>
</tr>
<tr>
<td>S15-B-3</td>
<td>444(445)</td>
<td>103</td>
<td>0.008(0.058)</td>
<td>0.66(0.67)</td>
</tr>
</tbody>
</table>

\(^a\): \(V\textsubscript{micro}\) micropore volume calculated from β\textsubscript{s} plot analysis; \(V\textsubscript{meso}\) mesopore volume calculated from β\textsubscript{s} plot analysis. These volumes, expressed in amounts of nitrogen gas adsorbed at standard temperature and pressure, were multiplied by the coefficient 0.001547 to be converted into liquid nitrogen volumes, as adsorbed at -196 °C (77K).

\(^b\): the values in brackets are theoretical ones calculated taking the titania weight into consideration, \(\text{Value}\textsubscript{meo}=\text{Value}\textsubscript{exp}/(1-\text{TiO}_2\text{ wt. %})\).

Figure 5.4.21 N\textsubscript{2} isotherms of S15-A-1, S15-A-2 and S15-0.
Figure 5.4.22 N₂ isotherms of mesoporous S15-B-2, S15-B-3 and S15-0.

Figure 5.4.23 Pore size distributions calculated using BJH model for S15-A-1 and S15-A-2.
Figure 5.4.24 Pore size distributions calculated using BJH model for S15-B-2 and S15-B-3.

BET surface areas and total volumes for two series of samples are listed in Table 5.4.3 together with the pore size values. With the increasing numbers of loading cycles, decreases in BET surface area and pore volume are clear but not significant for every titania-containing sample. However, considering the higher density of titania (Anatase, 3.84g/cm$^3$) compared with the silica (2.2g/cm$^3$), in fact, no significant net decrease in the surface area was found.

For A series, compared with the S15-0, BET surface area decreases from 793m$^2$/g for S15-0 to 724m$^2$/g for S15-A-1, while 612m$^2$/g for S15-A-2 was obtained. This indicates about 9% and 23% of the BET surface area were lost after loading titania of 10.2wt.% in S15-A-1 and 14.1wt.% in S15-A-2, respectively. Total pore volume of S15-A-1 decreases from 0.95cm$^3$/g for S15-0 to 0.87cm$^3$/g after incorporation of titania. And 0.81cm$^3$/g in S15-A-2 was found. However, theoretically calculated loss in BET surface area and pore volume is much smaller, as shown in Table 5.4.3. 90% of BET surface area for S15-A-2 remains while 14.1 wt.% of titania was anchored in
According to the $\beta_s$ plots analysis (Figure 5.4.25, 5.4.26 and Table 5.4.4), micropore volume of S15-A-1 of 0.064 are consistent with the theoretical value, 0.063, while $V_{\text{micro}}$ of S15-A-2 decrease significantly to 0.012 from 0.06, 80% lost. $V_{\text{meso}}$ of S15-A-1 and S15-A-2 are quite close to their theoretical values. Therefore, the disappearance of micropores and the preservation of mesopores can be explained as the filling of titania clusters into the micropores. The $\alpha_s$-plot analysis (Figure 5.4.29) further confirms the disappearance of micropores, as the $\gamma$-intercepts approximate to zero from S15-0 to S15-A-2.

For B series, compared with siliceous S15-0, 10% loss in BET surface area and 9% in pore volume of S15-B-2 were found. And similarly, 17% loss in BET surface area and 9% in pore volume of S15-B-3 were clear. The $A_{\text{meso}}$ of S15-B-2 and S15-B-3 calculated from the $\beta_s$ plot analysis (shown in Figure 5.4.27 and 5.4.28) were 463 and 444, respectively, indicating that 7% of total mesoporous surface area was lost for S15-B-2, whereas $A_{\text{meso}}$ was completely retained for S15-B-3. Therefore, the purpose for the maintenance of the mesoporous surface area was achieved in S15-B-3. Micropore volume dropped with increasing coating cycles. For S15-B-2, 85% of micropore volume remained and only 14% was remained for S15-B-3, indicating the disappearance of micropores. Mesopore volume for both S15-B-2 and S15-B-3 was quite close to the theoretical values. This demonstrated that the loading of titania into the micropores did not result in the change in mesopore surface area. In Figure 5.4.27, $\gamma$-intercepts are quite close for S15-0 and S15-B-2, while it approximates to zero for S15-B-3 (see Figure 5.4.28), indicating the disappearance of microporosity. The $\alpha_s$-plot analysis (Figure 5.4.30) also confirms these conclusions.

The loading of titania clusters into the micropores can also explain the phenomena observed from the low-angle XRD pattern. Accommodating small titania particles in micropores will cause the expansion in unit cell and pore size. Importantly, no blocking of mesopores was observed. In contrast, 10 wt.% of titania loaded MCM-41 also cause the blockage of mesopore [16]. Less than 12 wt.% of titania loading led to
the loss of almost half of BET surface area of mesoporous silica [17]. 40% of pore volume lost when 25wt.% titania was incorporated into MCM-41 [18].

From the calculation of pore size distribution using BJH model (shown in Figure 5.4.23 and 5.4.24), very sharp peaks for all the samples shows that the uniform distributed mesopores exist. The most probable distributed pore size are 7.67, 7.25, 7.73, 7.36nm for S15-A-1, S15-A-2, S15-B-2 and S15-B-3, respectively. It is obvious that pore shrinkages do happen with increasing titania content. Drops from 7.67 to 7.06nm for A series and from 7.73 to 7.36nm for B series were observed. Compared with the pore size of S15-0, the big increase after the first load cycle indicates the changes in the frameworks as confirmed by the XRD results. The filling of the titanium species expands the silica frameworks, leading to the increase in the d-spacings and pore walls. The pore size distributions are also narrow independent of titania content.

It is apparent that, for two samples in A series, significant decrease in micropore volume for S15-A-2, proves the filling of micropores. About 83% micropore volume of S15-0 (0.07cm\(^3\)/g) was lost after two cycles coating of titania for S15-A-2 (0.012cm\(^3\)/g). Similarly, only 14% was remained for S15-B-3. A conclusion can therefore be drawn that majority of the micropores were completely filled or blocked by the titania clusters introduced. This demonstrates the strategy assumed in this project is successful, i.e. loading of titania into the micropores leaving the most mesopore surface area unchanged.
Figure 5.4.25 $\beta_s$ plots analysis for S15-A-1.

Figure 5.4.26 $\beta_s$ plots analysis for S15-A-2.
Figure 5.4.27 $\beta_s$ plots analysis for S15-B-2.

Figure 5.4.28 $\beta_s$ plots analysis for S15-B-3
Figure 5.4.29 $\alpha_s$ plots analyses for (1) S15-A-1, (2) S15-A-2 and (3) S15-0.

Figure 5.4.30 $\alpha_s$ plots analyses for (1) S15-B-2, (2) S15-B-3 and S15-0.

The pore narrowing and even blocking may occur with the filling of titania into pores. Pore narrowing takes place when the titanium species are homogeneously dispersed on
the silica surface. Although, as discussed above, upon loading of increasing titania with more coating cycles, net loss in BET surface area and pore volume due to additional titania clusters are not significant, pore narrowing and blocking still need to be quantitatively discussed. It is noteworthy to note that the blocking effect for A and B series is primarily due to the blocking of micropores instead of the mesopores according to above discussions of N2-sorption results. Pore narrowing happens when the titania is grafted onto the inner surface of silica walls. However, the blocking due to the formation of big titania particles leading to pores inaccessible to N2 molecules may also take place with increasing coating cycles. The contribution of blocking and narrowing effects to the decrease in the pore volume were investigated. Table 5.4.5 gives the evaluation on pore narrowing and pore blocking.

Table 5.4.5 Evaluation on pore narrowing and pore blocking.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$V_p$ (exp.) ml/g</th>
<th>$V_p$ (theor.) ml/g</th>
<th>Blocking ml/g</th>
<th>Narrowing ml/g</th>
<th>Relative% blocking</th>
<th>Relative% Narrowing</th>
</tr>
</thead>
<tbody>
<tr>
<td>S15-0</td>
<td>0.95</td>
<td>0.95</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>S15-A-1</td>
<td>0.87</td>
<td>0.85</td>
<td>0</td>
<td>0.1</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>S15-A-2</td>
<td>0.81</td>
<td>0.82</td>
<td>0.01</td>
<td>0.13</td>
<td>7</td>
<td>93</td>
</tr>
<tr>
<td>S15-B-2</td>
<td>0.80</td>
<td>0.88</td>
<td>0.08</td>
<td>0.07</td>
<td>53</td>
<td>47</td>
</tr>
<tr>
<td>S15-B-3</td>
<td>0.72</td>
<td>0.79</td>
<td>0.07</td>
<td>0.16</td>
<td>30</td>
<td>70</td>
</tr>
</tbody>
</table>

a: The calculation methods are:

Column 3, $V_p$ (exp.) = $V_{pore} / (1 + w_{TiO_2})$, where $w_{TiO_2}$ is the weight percent obtained from the EDS analysis, and $V_{pore}$ for corresponding sample is listed in Table 5.4.4.

Column 4 loss of pore volume due to the blocking: subtract column 3 from column 2;

Column 5 is the difference between $V_{silica}$ and $V_{theor.}$.
Figure 5.4.31 Experimental pore volume of A series (■) compared with theoretical value (●) as a function of titania content in weight percent.

Figure 5.4.32 Experimental pore volume of B series (●) compared with theoretical value (▲) as a function of titania content in weight percent.
Chapter 5 Titania-containing mesoporous silica systems

The results of obtained $V_{\text{theor}}$ and experimental results are plotted against the titania containing per gram of silica, as shown in Figure 5.4.31 for A series and 5.4.33 for B series. From Figure 5.4.31, it can be seen that the pore volumes decrease linearly with the titania content, and that the experimental line is so close to the theoretical one for A series, suggesting that no blocking effects were observed. However, more apparent gaps for B series between the experimental and theoretical results can be found. This may assigned to more homogeneous dispersion of titania for A series than in B series. It is reasonable because the higher OH density for silica calcined at 120$^\circ$C for A series than that of B series, which is calcined at 300$^\circ$C. Therefore, the growth of titania particles are more significant for B series than A series. Such conclusion could be supported by the Raman and UV-DRS spectra of two series samples.

Additionally, the sample after two cycles coating were also examined. The $N_2$ physisorption data using similar mesoporous silica–SBA-15 (designated as S15-C-2, detailed synthesis parameters are shown in Table 5.3.1) is shown in Figure 5.4.33. Clearly, type H1 desorption hysteresis loop, as recommended in IUPAC manual, appears in the vertical portion of the type IV nitrogen isotherm, characteristic of the mesoporous material with cylindrical pores. Importantly, broad and square-shaped loop indicative of a type H2 hysteresis loop was not identified in this isotherm. Although the interpretation of this type of hysteresis loop is the subject of some debate, it is commonly connected with 'ink bottle' shaped pores, in which the area near the opening is narrower than the main body of the pore [53]. This further supports that the dispersion of titania is homogeneous in the whole system via the MSI method.
Figure 5.4.33 $N_2$ absorption-desorption isotherm and pore distributions of S15-C-2.

5.4.4 MSI method and OSI method

For comparison, a titania-containing SBA-15 was also synthesized using OSI method (designated as S15-D-1, see Table 5.3.1). The $N_2$ physisorption data and pore distributions are shown in Figure 5.4.34. Distorted H1 hysteresis loop indicates the changes in the mesostructures. The BJH pore size decreases to 5.4nm, revealing the significant narrowing or even the blocking of mesopores compared with afore-mentioned samples. The $\beta_v$ plot analysis (Figure 5.4.35) shows that the pore volume of S15-D-1 decreases to 0.49cm$^3$/g. Theoretical value without blockage is 0.68 cm$^3$/g. This means that almost 30% of the pore volume of starting mesoporous SBA-15 silica was lost due to the blockage.

Additionally, direct evidence of blockage of mesopore was given by TEM measurement. Figure 5.4.36 shows the TEM of S15-D-1. It can be seen from this figure that the formed bigger titania particles exceed the mesopore size and are responsible for the blockage. Figure 5.5.4.38 shows the wide-angle XRD pattern for S15-D-1. It is clear that the titania particles are also big enough to give XRD
reflections corresponding to anatase phase. UV-vis-DRS spectra of S15-D-1 (see Figure 5.4.38) shows that the absorption edge of S15-D-1 approximates to that of bulk titania. This attests the presence of bulk titania particles. The particle size is estimated to around 4nm.

It is believed that the residue TTIP during the synthesis of S15-D-1 may decompose and contribute to the growth of titania particles even after only one coating cycle. Apparently, loading high amount of titania via OSI method causes the excessive growth of titania phase and thus the blockage of mesopores. In contrast, for the MSI method, in each cycle of loading, self-limiting reactions between TTIP molecules with homogeneously dispersed surface hydroxyls guarantee high dispersion of titania species. Especially, the residue TTIP molecules are also vacuumed away minimising the growth of titania particles.

![Figure 5.4.34 N2 absorption-desorption isotherm and pore distributions of S15-D-1.](image)

Figure 5.4.34 N2 absorption-desorption isotherm and pore distributions of S15-D-1.
Figure 5.4.35 $\beta_s$ plot analysis of S15-D-1.

Figure 5.4.36 TEM photograph of S15-D-1.
Figure 5.4.37 Wide-angle XRD pattern for S15-D-1.

Figure 5.4.38 UV-vis DRS spectra of S15-D-1, the inset is the plots of $(F(R_{sh})*h\nu)^{1/2}$ against photo energy of S15-D-1.

In our experiments, the amount of titania picked up on/in the mesostructures actually depends on the OH density on the silica surface. After comparing more than 100 kinds
of silica, Zhurravlev et al [54, 55] has drawn a conclusion that the $\alpha_{OH}$ can be thought as a physical-chemical constant for a fully hydroxylated surface and the value of $\alpha_{OH}$ is only the function of temperature and does not depend significantly on the type of silica. The total number of hydroxyl groups ($\alpha_{OH}$) on the silica surface is shown in Table 5.4.6.

<table>
<thead>
<tr>
<th>T/K</th>
<th>$\alpha_{OH}$ nm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>373</td>
<td>5.0</td>
</tr>
<tr>
<td>473</td>
<td>4.7</td>
</tr>
<tr>
<td>573</td>
<td>3.4</td>
</tr>
<tr>
<td>673</td>
<td>2.2</td>
</tr>
<tr>
<td>773</td>
<td>1.8</td>
</tr>
<tr>
<td>873</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Therefore the $\alpha_{OH}$ for the starting pure mesoporous silica SBA-15 is 5.0 and 3.4 per nm$^2$ for A series and B series, respectively. The reaction between titanium alkoxide with surface hydroxyl groups (isolated OH or hydrogen-bonded OH) is self-limiting on the condition that there is no excess or physically adsorbed water on the silica surface, so that the capacity to pick up the titania for these two series should be different on varied silica pretreated at different temperatures. Therefore, complete consumption of surface hydroxyls will lead to different titania content. This can be seen from the amount of titania incorporated in A series and B series of samples. One loading cycle introduced 10.2 wt.% of titania into S15-A-1 in comparison with 7.5 wt.% for S15-B-2 after two cycles. Not surprisingly, in the third cycle S15-A-3 picked up 24.4 wt.% of titania, while only 17.1 wt% for S15-B-3.

When free water or excess of TTIP are present, more titania will be anchored and the growth of titania particle is unavoidable. Grieken et al [22] synthesized titania containing SBA-15 by controlling titania particles size in the mesochannels. However,
free titania precursors were not removed and then further hydrolyzed to form bigger titania particles comparative to the mesopore (6-8nm) after the calcination.

There are several possibilities in the distribution of titanium species in the mesopores: (1) homogeneous and smooth layer formed on the surface of silica; (2) irregular dispersion of titanium species, such as free Ti-OH and titania nanoclusters; (3) bigger agglomerates blocking the mesopores; and (4) island-like nano-sized titania particles evenly dispersed throughout the samples. The first possibility can be rule out by N₂ adsorption (the existence of micropores) and FTIR results (the surface silanols are almost intact compared with starting SBA-15). No significant reduction in XRD low-angle reflections and no bigger titania particles in TEMs using magnification of 150K were found. The formed titania particles should be less than 3nm so that no wide-angle in XRD can be identified. The blue shifts of band edges or the increasing the bandgap energy in UV-vis DRS spectra show that the titania particles should be very small—estimated to be about 1.3nm.

![Figure 5.4.39 Schematic for the filled SBA-15 by TiO₂. (A) SBA-15 and (B) titania (black spots)-containing SBA-15.](image)

In fact, from the results of N₂ adsorption data, small titania clusters were, to a great extent, entrapped in the micropores connecting the mesopores in the walls, as schematically shown in Figure 5.4.39, leaving the mesopore unblocked.
In a word, the micropores in S15-0 disappeared in S15-B-3 and S15-A-2 can be interpreted by the filling of nano-sized titania clusters in the micropores. The mesopores are left unblocked. Better dispersion in A series can be found. No bottle-shaped hysteresis loop was found in samples synthesized using the same method. For samples synthesized via OSI method, blocking of mesopores by bigger titania particles were observed. This further proves that the MSI method is effective to incorporate high amount of titania into SBA-15 without blocking the mesopores.

5.4.5 Titania chemical nature of TiO2-containing SBA-15

More and further information about the chemical states and interactions of titania species with silica can be furnished by XPS and FTIR measurements. XPS is widely used in catalysis because it allows the determination of the chemical state of the elements of the solid surface. In this section, S15-B series are selected as examples to illustrate the chemical nature of titania incorporated.

Figure 5.4.40 XPS spectra of (1) S15-B-2 and (2) S15-B-3.

Figure 5.4.40 shows the XPS spectra of S15-B-2, 3. It can be seen from this figure that the titanium species are present on the surface of samples. The third cycle coating led
to more resolved peaks corresponding to the Ti 2p photoelectron peak. A trace of carbon was also detected. No other peaks can be seen in the spectra.

In the Ti-Si binary oxide system, the formation of Ti-O-Si bands has been extensively investigated, such as titanium-substituted mesoporous silica [56-64], titania-coated mesoporous silica [65-70] and so on. In the Ti-substituted mesoporous silica, the Ti$^{4+}$ species are normally incorporated into the silica framework, in which it is believed to be in tetrahedral or distorted tetrahedral coordination in the molecular sieves through the bonds of Ti-O-Si. The Ti-O-Ti linkages are not present or only a few. In the samples synthesized by employing the post-synthetic approaches, situations are more complicated, depending on the methods assumed, titanium species content, and experimental conditions. Method of atom planting using TiCl$_4$ favours the formation of anatase phase, while the samples synthesized using grafting technique showed the presence of very small clusters [65]. Higher titania content reaching to 20wt.% led to the formation of anatase particles with the size larger than 6nm [68].

**Figure 5.4.41** Deconvolutions of O 1s peaks for S15-B-2 recorded for a takeoff angle of 90° with respect to surface normal. The left one is deconvoluted as three peaks, at 533.05, 531.7, and 530.2, while 533.05 and 530.2 for the right one.
In our case, samples were synthesized using the impregnation method. The highest titania content was up to 17.1%. Information on the surface, for example the surface atom ratio, electronic structure, can be derived from XPS measurements. Figure 5.4.41 shows the XPS spectra of S15-B-2. The O 1s core lines of sample S15-B-2 with the take-off angle of 90 degrees are recorded and then are carefully deconvoluted into several peaks corresponding to O 1s in pure bulk titania (530.2eV), pure silica...
(533.05eV) and Ti-O-Si bonds (531.7) on the base of published binding energy shifts for SiO₂, TiO₂ and SiO₂/TiO₂ mixed oxides systems [71-73]. It is clear that the fittings without peak located at 531.7eV are not good, as shown in Figure 5.4.41 (right). However, the introduction of a new peak at 531.7eV, assigned to the oxygen in Ti-O-Si cross-linking bonds, leads to very good fitting (Figure 5.4.41, left), demonstrating the presence of Ti-O-Si bonds in the interphases. Therefore, the strong interactions via the Si-O-Ti bonds between titania phase and silica base exist. This is in good agreement with a decrease in the negative charge of the oxygen (or a decrease in the polarizability) and a decrease in the ionic nature of the bonds at the interphases compared with the Ti-O-Ti in bulk titania. Compared with the O 1s core line recorded using the take-off angle of 30 degrees (Figure 5.4.42, middle), using smaller take-off angle, 30° in our case, has little influence on enhancing the surface sensitivity.

Table 5.4.7 Results of fitting analysis of O 1s peaks in Figure 5.4.42.

<table>
<thead>
<tr>
<th>Samples</th>
<th>P(Ti-O-Ti (530.2))</th>
<th>P(Si-O-Ti (531.7))</th>
<th>P(Si-O-Si (533.05))</th>
<th>Surface Atom ratios(Ti/Si)</th>
<th>Bulk Ti/Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>S15-0</td>
<td>0</td>
<td>0</td>
<td>1.00</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>S15-B-1</td>
<td>0.028 (223.9)</td>
<td>0.17 (1350.9)</td>
<td>0.802 (6408.3)</td>
<td>0.048</td>
<td>0.045</td>
</tr>
<tr>
<td>S15-B-2</td>
<td>0.088 (163.6)</td>
<td>0.13 (239.8)</td>
<td>0.782 (1440.5)</td>
<td>0.063</td>
<td>0.063</td>
</tr>
<tr>
<td>S15-B-3</td>
<td>0.093 (310.2)</td>
<td>0.15 (508.0)</td>
<td>0.757 (2527.7)</td>
<td>0.1</td>
<td>0.156</td>
</tr>
</tbody>
</table>

a: P means the percentage of the peak areas (in the brackets); b: The surface atomic ratios were obtained by correcting the intensity ratios with theoretical sensitivity factors proposed by the manufacturer; c: the bulk surface atomic ratios of Ti to Si were calculated from the actual TiO₂ concentration.
The deconvolutions of O 1s peaks recorded using the take-off angle of 30 degrees was also done. The results are shown in Figure 5.4.42. Besides the Ti-O-Ti linkages and Si-O-Si in the silica base, the Si-O-Ti cross-linking did happen in the interphases, as discussed above. The formation of Ti-O-Ti linkages in the sample of S15-B-1, although only a few, (with least titania content) can be seen from the Figure 5.4.42. With increasing coating cycles, these phases are more prominent, revealing the growth of titania nano-domains. This can also be seen from Table 5.4.7, where the percentages of Ti-O-Ti bonds increase steadily from 0.028 to 0.093, while the Si-O-Ti bonds in the interphase remain constant — in the range of 0.15±0.02. The percentages of Si-O-Si slightly decreases from 0.802 to 0.757 as expected because more of titania species were incorporated. This can be interpreted as the growth of titania phases and is in good correlation with the results of N₂ adsorption and UV-vis measurements. It is worthy to note that the presence of absorbed water (the peak at 534.1eV) is clear in the sample S15-B-2, as shown in Figure 5.4.42, middle ones [74]. This leads to the broadening of the O 1s core line, compared with the other two samples of S15-B-1 and
3, which are degassed at room temperature for 3 hours before measurements. The surface and bulk atomic ratios of Ti to Si on the surface were also examined. As shown in Table 5.4.7 and Figure 5.4.43, the Ti/Si atomic bulk ratios vs Ti/Si surface atomic ratios show a linear relationship up to TiO_2 wt. 7.5% with a slope equal to 1, indicating relatively highly dispersion of Ti atoms on/in the silica matrix. The surface Ti/Si ratios are consistent with those of bulk Ti/Si ratios. However, for the samples after three coating cycles, reduced levels of titanium could be detected by XPS, indicating that some of Ti atoms could reside in pores and escape the detection. This is in quite good agreement with the results of N₂ adsorption results, which indicates that the micropores in the most parts were blocked by the titania small clusters.

XPS results suggest that, besides the formation Ti-O-Ti phases, Si-O-Ti bonds also exists in the interphases. Ti/Si surface atom ratios show that dispersion of titania in S15-B-1 and S15-B-2 is higher than S15-B-3, in which much of Ti atoms reside in pore beyond the detection of XPS. However, more evidence can be obtained by FTIR measurement.

Figure 5.4.44 FTIR spectra for the four samples without heating pre-treatment: (1) S15-B-1, (2) S15-B-2, (3) S15-B-3, and (4) S15-0.
Figure 5.4.45 $\delta_{\text{OH}}$ and SiO bands in FTIR spectra of the four samples pre-treated at 373K for 2h, (1) S15-B-1, (2) S15-B-2, (3) S15-B-3, and (4) S15-0.

Figure 5.4.46 $\nu_{\text{OH}}$ stretching bands in FTIR spectra for the four samples pre-treated at 373K for 2h: (1) S15-B-1; (2) S15-B-2; (3) S15-B-3; and (4) S15-0.
Figure 5.4.47 $\delta$OH and SiO bands in FTIR spectra of the four samples pre-treated at 473K for 2h: (1) S15-B-1, (2) S15-B-2, (3) S15-B-3 and (4) S15-0.

Figure 5.4.48 $\nu_{OH}$ stretching bands in FTIR spectra of the four samples pre-treated at 473K for 2h: (1) S15-B-1, (2) S15-B-2, (3) S15-B-3 and (4) S15-0.
Figure 5.4.49 The $\delta_{\text{OH}}$ and SiO bands in FTIR spectra of the four samples pre-treated at 673K for 2h: (1) S15-B-1, (2) S15-B-2, (3) S15-B-3 and (4) S15-0.

Figure 5.4.50 The $\nu_{\text{OH}}$ stretching bands in FTIR spectra of the four samples pre-treated at 673K for 2h: (1) S15-B-1, (2) S15-B-2, (3) S15-B-3, and (4) S15-0.
Infrared spectroscopy provides important information in the lattice vibrations of the mixed oxides and has also been extensively used. Two regions of $v_{\text{OH}}$ stretching bands and $\delta_{\text{OH}}$ and SiO bands shown in Figure 5.4.44 to Figure 5.4.50 were investigated separately.

In the $\delta_{\text{OH}}$ range, bands at about 810 cm$^{-1}$ and 1090 cm$^{-1}$ (shown in Figure 5.4.44) are assigned to the symmetry and asymmetry stretching vibrations of SiO$_4^{4-}$ structural units. Sharp bands at around 463 cm$^{-1}$ correspond to the Si-O-Si or O-Si-O bending mode. In the pure silica, S15-0, without drying (Figure 5.4.44) or dried at 100 for 2h (Figure 5.4.45), peaks at about 965 (due to the perturbation of surface absorbed water) and 975 cm$^{-1}$ can be clearly seen, respectively, which is ascribed to the stretching of the Si-O- defect sites, the stretching vibration of free silanol groups on the surface of silica. The bands at about 975 cm$^{-1}$ still exist in S15-0 as shown in Figure 5.4.49, and
position of this band is independent of the calcination temperature. Some researchers have used the band at about 960\,cm\(^{-1}\) as the evidence for the presence of Ti-O-Si bonds or semi-quantitatively analysis of the degree of Ti-O-Si hetero-linkages in titania-silica samples [75-81]. This should be questionable as proved in Figure 5.4.44, 45 and 5.4.47. However, in samples calcined at elevated temperatures, the shifts from 975\,cm\(^{-1}\) to 944 \,cm\(^{-1}\) can be observed compared with the pure silica, which was calcined under the same condition. The calcination, therefore, can play an important role to distinguish the contributions from the Si-OH groups and other Si-O- defects (in our case, the Si-O-Ti bonds). The deconvolutions (shown in Figure 5.4.51-53) of the peaks in the \(\delta_{\text{OH}}\) range of S15-B-1, 2, 3 were carried out. The peaks centred at about 960\,cm\(^{-1}\) were divided into two peaks. One is at 974\,cm\(^{-1}\) corresponding to the silica defects sites—surface silanols, and the other is at 944\,cm\(^{-1}\) due to the formation of Si-O-Ti bonds [60]. Combining the shifts of the peaks and the deconvolution, it is more convincing and logical that the formation of Si-O-Ti occurred.

![Figure 5.4.52 Deconvolution of the \(\delta_{\text{OH}}\) and SiO bands in FTIR spectra of S15-B-1.](image)
In the νOH stretching region, the peaks at 3740 cm\(^{-1}\) increased with higher calcination temperatures, as shown in Figure 5.4.46, 5.4.48 and 50, which are ascribed to the isolated SiOH on the silica surface [82-86]. The higher temperature (from 373K to 673K), the more prominent the peaks are. X. S. Zhao et al [87] have reported that isolated Si-OH groups on silica surface modified with TRMS were consumed as the 3740 cm\(^{-1}\) peak disappeared. K. Schrijnemakers, et al [82] also reported the weakening of this peak after the deposition of titania onto the silica. In our case, the existence of free Si-OH groups in the titania-SBA-15 is clear. However, no significant decreasing of this peak were observed, compared with the siliceous S15-0. The coating of titania, which did use the surface Si-OH groups to anchor the titanium precursors, did not influence Si-OH groups at all. One reason is that, as proposed by Srinivasan et al [88], hydrogen-bonded hydroxyls are more reactive at room temperature than isolated hydroxyls. So the titania species are more likely immobilized by the hydrogen-bonded Si-OH, leaving isolated Si-OH almost intact. At least from the results of FTIR, this

**Figure 5.4.53** Deconvolution of the δOH and SiO bands in FTIR spectra of S15-B-2.
possibility cannot be ruled out. Another reason is that the formation of small titania nano-domains are favoured during the calcination process. Results of FTIR (see above and below discussions), XPS (showed that increasing Ti-O-Ti linkages exist with increase in the titania content), UV-vis (formation of Ti-O-Ti cross-linking did happen) show that small titania clusters were formed. Therefore, the titania species were not homogeneously dispersed as monolayer coating on the silica surface. In fact, from the results of N2 adsorption data, small titania clusters were, to a great extent, entrapped in the micropores connecting the mesopores in the walls.

Figure 5.4.54 The difference spectra in the δ_OH region of FTIR spectra for (1) S15-B-1, (2) S15-B-2, and (3) S15-B-3.

Peaks at 944cm⁻¹ and 657cm⁻¹ are also fairly clarified in the difference spectra in Figure 5.4.54, obtained by subtracting the spectrum of the reference spectra of silica S15-0. Interactive subtractions were performed. A different f was chosen in order to make the bands belonging to symmetric νSi-O-Si stretching vibrations as close as possible (f₁, f₂, f₃, use to multiply the data of S15-B-1, 2 and 3 are 0.98, 0.92 and 1, respectively). The broad peak at around 657cm⁻¹ increases with number of coating
cycles correlating with the amount of titania species picked up, which can be attributed to the titania nanophases [87, 89]. This is in good agreement with results of XPS, UV-vis DRS, and N\textsubscript{2} adsorption measurements — the growth of the titania nanoclusters. The peaks at 944 cm\textsuperscript{-1} remain unchanged. This can be interpreted as the growth of titania nano-domains instead of steadily forming more Si-O-Ti bonds.

The bands deconvoluted in Figure 5.4.51-53 can be used for the semi-quantitative estimation of Si-O-Ti connectivity (D\textsubscript{Si-O-Ti}). The positions and the assignments of these vibrations are as follows: 944 cm\textsuperscript{-1} corresponding to ν\textsubscript{Si-O-Ti} vibrations as discussed above, bands at about 1080 cm\textsuperscript{-1} corresponding to asymmetric ν\textsubscript{Si-O-Si} stretching vibrations [90], bands at about 1166 and 1225 cm\textsuperscript{-1} corresponding to symmetric ν\textsubscript{Si-O-Si} stretching vibrations [91-93]. The estimation of Si-O-Ti connectivity, D\textsubscript{Si-O-Ti}, is defined as

\[ D_{\text{Si-O-Ti}} = \frac{S_{\text{Si-O-Ti}}}{S_{\text{Si-O-Si}}} \times \frac{x_{\text{Si}}}{x_{\text{Ti}}} \]

\( S_{\text{Si-O-Ti}} \) and \( S_{\text{Si-O-Si}} \) are the deconvoluted peak areas of the ν\textsubscript{Si-O-Ti} at 944 cm\textsuperscript{-1} and ν\textsubscript{Si-O-Si} at 1225 cm\textsuperscript{-1}, respectively. \( x_{\text{Si}} \) and \( x_{\text{Ti}} \) are the molar proportions of Si and Ti. Such D\textsubscript{Si-O-Ti} values are supposed to represent a semi-quantitative measure of the proportion of Si-O-Ti species with regard to the total Ti content. The higher the D\textsubscript{Si-O-Ti} values are, the higher dispersion of titania species. The results are listed in Table 5.4.8.

It is clear that D\textsubscript{Si-O-Ti} decreases with the increasing loading cycle from 6.4 for S15-B-1 to 2.5 for S15-B-3. It is apparently that dispersion of titanium species in S15-B-1 is higher than that in S15-B-3. The proportion of Si-O-Ti species referred to the total Ti content decreased upon loading more of titania. The dispersion of titanium species is simply homogeneous, i.e. monolayer coating of titania onto the silica support via Si-O-Ti bonds.
Table 5.4.8 $D_{\text{Si-O-Ti}}$ connectivity of the TiO$_2$-containing SBA-15

<table>
<thead>
<tr>
<th>Samples</th>
<th>S15-B-1</th>
<th>S15-B-2</th>
<th>S15-B-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ratios of $S_{244}/S_{1225}$</td>
<td>0.29</td>
<td>0.35</td>
<td>0.4</td>
</tr>
<tr>
<td>Ratios of bulk Si/Ti</td>
<td>22.2</td>
<td>15.9</td>
<td>6.4</td>
</tr>
<tr>
<td>$D_{\text{Si-O-Ti}}$</td>
<td>6.4</td>
<td>5.6</td>
<td>2.5</td>
</tr>
</tbody>
</table>

In comparison, in some TiO$_2$-SiO$_2$ mixed oxides, such as TS-1 (with ca. 2.4 at% Ti or less) [94], whose titania dispersion is atomically mixed with silica (or molecular-scale mixing of titania and silica), the $D_{\text{Si-O-Ti}}$ is up to 17, which is much higher than that of S15-B-1. However, some Ti-O-Ti structural units were confirmed to be present in samples besides the atomically mixed titanium, whose $D_{\text{Si-O-Ti}}$ is lower than 17. Some small particles about 8nm were observed in samples whose $D_{\text{Si-O-Ti}}$ values are less than about 3 [95, 96]. In our case, $D_{\text{Si-O-Ti}}$ of all the three samples is lower than 17, indicating the formation of some Ti-O-Ti structural units. With the increase in titania content, the $D_{\text{Si-O-Ti}}$ is lower than 3 for S15-B-3, revealing the formation of titania nano-domains. $S_{244}/S_{1225}$ values increase from 0.29 to 0.40, indicating the slight increase in quantity of Si-O-Ti bonds with increasing titania content. As discussed above, however, the proportion of Si-O-Ti bonds with reference to the total titania content decreased from S15-B-1 to S15-B-3. This is in good agreement with the results of XPS, and UV-vis DRS. The Ti-O-Ti species tend to form the titania nanoclusters instead of Si-O-Ti bands on the silica support.

From the FTIR results, Ti-O-Ti nanophases and Si-O-Ti bonds co-exist in S15-B-3, which agree with XPS results very well. Moreover, FTIR further demonstrates that with the increase of titania content, Si-O-Ti bonds increase in quantity but decrease in proportion of Si-O-Ti bonds with regard to the total titania content.

5.4.6 Thermal and hydrothermal stability of TiO$_2$-containing SBA-15

Hydrothermal and thermal stability of these samples were also examined. Figure 5.4.55-57 show the TEM of S15-A-2 treated at different temperatures in the air. TEMs
of S15-A-2 treated at different temperatures are quite similar to each other. Raman spectra were also collected and shown in Figure 5.4.58. From this Figure, it can be seen that the agglomeration is not serious upon calcination at 700°. The UV-vis-DRS measurements were also carried out and the results are shown in Figure 5.4.59 and 60. The changes in the absorption edges in Figure 5.4.60 can be interpreted by the dehydration or de-hydroxyls of S15-B-2 at high temperatures [97]. It is clear that calcination at 500, 600 and 700° has no significant influence on the growth of titania phase, which can also be seen according to the Raman results. Therefore, the thermal stability of titania-containing SBA-15s is good.

**Figure 5.4.55** TEM photograph of S15-A-2 calcined at 773K.
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Figure 5.4.56 TEM photograph of S15-A-2 calcined at 873K.

Figure 5.4.57 TEM photograph of S15-A-2 calcined at 973K.
Figure 5.4.58 Raman spectra of S15-B-2 calcined at (1) 500, (2) 600, and (3) 700°C.

Figure 5.4.59 Diffuse reflectance UV-vis spectra of S15-B-2 calcined at (1) 673K, (2) 773K, (3) 873K, (4) 973K and (5) room temperature.
Figure 5.4.60 Plots of $(F(R_\infty)^2/hv)^{1/2}$ against photo energy of S15-B-2 calcined at (1) 673K, (2) 773K, (3) 873K, (4) 973K and (5) room temperature.
Figure 5.4.61 TEM photograph of hydro-thermally treated S15-B-3.
Figure 5.4.62 TEM photograph of hydro-thermally treated S15-B-3.
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Figure 5.4.63 Raman spectra of hydrothermal treated S15-B-3.

Figure 5.4.64 Plot of \((F(R_\infty)\cdot hv)^{1/2}\) against photo energy of hydrothermally treated S15-B-3.

Figures 6.4.62 and 5.4.63 show the TEM photographs of hydro-thermally treated S15-B-3. After the hydrothermal treatment, the formation of big extra-framework titania particles are also clearly visible in these TEMs. Hydrothermal treatment in
boiling water was found to be capable of breaking the bonds of Si-O-Ti [59, 60] and then promoting the formation of more titania phase. Figure 5.4.63 shows the Raman spectra of hydro-thermally treated S15-B-3. It can be seen from this figure that the hydro-thermally-treated S15-B-3 shows the presence of crystalline anatase TiO₂ as the results of breakages of Si-O-Ti bonds to release Ti-O species for the growth of titania phases. Figure 5.4.64 shows the plot of \((F(R_\alpha)h\nu)^{1/2}\) against photo energy of hydrothermally treated S15-B-3. It can be seen that the band-gap energy is about 3.33eV, which is quite close to that of the bulk titania. This further demonstrates the formation of bulk titania phase. This is in good agreement with the results of Raman, TEM results. This means the hydrothermal stability is not satisfied for such titania-containing SBA-15.

5.5 Photocatalytic performance

In above sections, titania-containing mesoporous silicas were investigated by means of various techniques including their characterisation in terms of mesostructural ordering after loading titania, chemical nature of the titania species incorporated, thermal and hydrothermal stability and so on. As introduced in Section 5.1, it is important to synthesize 'clogging-free' titania-containing mesopore silica. Therefore, in this section, the photo-activities for destructing organic pollutants of titania-containing mesoporous silica synthesized by the MSI method will be studied.

Phenol and its derivatives are widely distributed contaminations of natural waters and wastewaters. Especially, phenol is hard to degrade. In recent years, there is also an increasing concern over the endocrine disrupting effect of the endogenous estrogens and xenoestrogens in environmental water through the excretions of humans, domestic, farm animals and so on. Among the endogenous oestrogens, estradiol shows the highest estrogenic potential, which is found in many water systems, such as rivers and effluent from sewage treatment plants [98-100]. Thus, photo-degradation behaviour of the three organics by the catalyst synthesized was investigated.
5.5.1 Mechanism of photocatalytic process in TiO₂

Unlike metals which have a continuum of electronic states, semiconductors possess a void energy region where no energy levels is available to promote recombination of an electron and hole produced by photo-activation in the solid. This photo-activation process could happen only when a photon with the energy $hν$ matches or exceeds the band-gap energy $E_g$ of the semiconductor. As a result, an electron, $e_{vb}^-$, is promoted from the valence band, VB, into the conduction band, CB, leaving a hole, $h_{vb}^+$ behind (Figure 5.5.1, the enlarged part). The void region which extends from the top of the conduction band to the bottom of the valence band is called the band-gap. The excited state conduction band electrons and valence band holes can recombine and dissipate the input energy as heat, get trapped in metastable surface states, or react with reductants and oxidants adsorbed on the semiconductor surface, as shown in Figure 5.5.1 [42]. It can be seen from this figure that recombination of generated electrons and holes can happen on the surface (pathway A) or in the volume of the semi-conductor particle (pathway B) with the release of heat. Moreover, the generated electrons, after migrating to the surfaces, can reduce an electron acceptor (pathway C) and, in return, the holes can migrate to the surface for oxidising a donor species (pathway D).

Figure 5.5.1 Schematic photo-activation in a semi-conductor particle [98].
As proposed by Hoffmann et al. [101], the mechanism of photocatalysis on the TiO\textsubscript{2} is as follows:

**Charge carrier generation:**
\[
\text{TiO}_2 + h\nu \rightarrow h^+ + e^-
\]

**Charge carrier trapping:**
\[
e^+ + \text{Ti}^{IV}\text{OH} \rightarrow (>\text{Ti}^{III}\text{OH})
\]
\[
h^+ + \text{Ti}^{IV}\text{OH} \rightarrow (>\text{Ti}^{IV}\text{OH})^+
\]

**Charge carrier recombination:**
\[
h^+ + e^- \rightarrow \text{thermal energy}
\]
\[
e^+ (>\text{Ti}^{IV}\text{OH})^+ \rightarrow \text{Ti}^{IV}\text{OH}
\]
\[
h^+ (>\text{Ti}^{III}\text{OH}) \rightarrow \text{Ti}^{IV}\text{OH}
\]

**Interfacial charge transfer:**
\[
 (>\text{Ti}^{IV}\text{OH})^++\text{Red} \rightarrow \text{Ti}^{IV}\text{OH} + \text{Red}^{++}
\]
\[
 (>\text{Ti}^{III}\text{OH}) \rightarrow \text{Ti}^{IV}\text{OH} + \text{Ox}^{-}
\]

Where \( h\nu \) is UV photon, >\text{TiOH} represents the hydrated surface functional group, (\text{Ti}^{III}\text{OH}) is the surface-trapped conduction electron while (>\text{Ti}^{IV}\text{OH})\text{^+} is the surface-trapped valence band hole, Red is a reductant and Ox is an oxidant.

5.5.2 Photocatalytic performance of TiO\textsubscript{2}-containing mesoporous silica

The photocatalytic activities for degradation of salicylic acid were examined. Figures 5.5.2 and 5.5.3 show the plots of concentration of salicylic acid vs irradiation time in S15-A-1, 2, and 3 and S15-B-1, 2, and 3 systems for photo-degradation of salicylic acid, respectively. For both A and B series, not only S15-A-2 and S15-A-3 but also S15-B-2 and S15-B-3 show similar photocatalytic activity. It is also clear that the photo-activity increases with increasing titania loading. For all the samples, adsorption of salicylic happened in the starting period and then the concentration of salicylic acid decrease linearly afterwards. The absorption of salicylic acid was also confirmed under condition that no irradiation and prolonged time of 20 hr was employed. As shown in Figure 5.5.4, S15-B-3 and pure mesoporous silica do adsorb salicylic acid with the former slightly absorbing more. According to the results shown in Figures 5.5.2 and
5.5.3, the balance of adsorption seems to be reached in two hours. S15-D-1 shows the best performance in decomposing salicylic acid in water. After 8 hours' irradiation, almost 90% salicylic was decomposed.

Figure 5.5.2 Plots of concentration of salicylic acid vs. irradiation time in S15-A-1, 2, 3, S15-D-1 systems.

Figure 5.5.3 Plots of concentration of salicylic acid vs. irradiation time in S15-B-1, 2, 3 systems.
Figure 5.5.4 Column graphs of adsorption test of salicylic acid in S15-B-3 and S15-0 systems (stored in dark for 20hr).
The photocatalytic activities for degradation of phenol were also studied. Figures 5.5.5 and 5.5.6 show the plots of concentration of phenol vs. irradiation time in S15-A-1, 2, 3, and S15-B-1, 2, and 3 systems, respectively. Unlike salicylic acid, no adsorption of phenol on mesoporous catalysts was observed. From Figures 5.5.5 and 5.5.6, it can be seen that, with the increasing titania content, photocatalytic activity clearly increases for B series. A series show better performance than B series due to their higher titania contents. Similarly, performance of S15-D-1 turns out to be the best for the degradation of phenol in water. Additionally, presences of p-benzoquinone and hydroquinol at 244nm and 295nm was also observed, respectively. Changes in the relative concentration of p-benzoquinone and hydroquinol were monitored and the results are shown in Figures 5.5.7 and 5.5.8, respectively. With increasing irradiation time, the concentrations of p-benzoquinone and hydroquinol for S15-A series S15-B-3 increase rapidly in 4 hours and then keep constant. For S15-D-1, these intermediates
were also decomposed after 4 hours' irradiation. This further attests for the good performance of S15-D-1 in complete decomposing and further mineralising phenol in water.

Figure 5.5.7 Plots of absorption of p-benzoquinone vs. irradiation time in S15-A-1, 2, 3, S15-B-3, and S15-D-1 systems, respectively.

Figure 5.5.8 Plots of absorption of hydroquinol vs. irradiation time in S15-A-1, 2, 3, S15-B-3, and S15-D-1 systems, respectively.
Figure 5.5.9 Plots of concentration of oestrogen vs. irradiation time in S15-A-3, S15-B-3, and S15-D-1 systems, respectively.

Figure 5.5.10 Column graphs of adsorption test of oestrogen in S15-B-3 and S15-0 systems, respectively (stored in dark for 20hr).
Figure 5.5.11 Plot of concentration of oestrogen vs. irradiation time in bulk titania (25nm) system.

Figure 5.5.12 Plots of oestrogen destructed normalized by titania content vs. irradiation time in (1) S15-D-1, (2) bulk titania (25nm), (3) S15-A-3, and (4) S15-B-3 systems, respectively.
The tests of photo-degradation of oestrogen in water/ethanol mixtures were also performed. S15-A-3, S15-B-3 and S15-D-1, which show good catalytic performances in decomposing salicylic acid and phenol in water, were selected for decontamination of oestrogen. Figure 5.5.9 shows concentration changes of oestrogen (the absorptions were determined at 280.6nm) vs irradiation time in S15-A-3, S15-B-3 and S15-D-1 systems. S15-A-3 shows the highest performance in decomposing the oestrogen in water/ethanol mixture. S15-D-1, which proved to be active in decontaminating phenol and salicylic acid, shows almost no activity. Additionally, as shown in Figure 5.5.10, there is negligible adsorption of oestrogen on the mesoporous silica or titania-containing mesoporous silica. For comparison, photocatalytic properties of bulk titania catalyst were also examined. It is clearly shown in Figure 5.5.11 that, after 8 hr irradiation, about 13% of oestrogen was degraded. Figure 5.5.12 plots of oestrogen destructed normalized by titania content against irradiation time. Average specific reaction rate normalized by the amount of titania utilized for S15-A-3, S15-B-3 and bulk titania are $1.73 \times 10^{-5}$, $1.53 \times 10^{-5}$ and $1.20 \times 10^{-5}$ mol g$^{-1}$ h$^{-1}$, respectively. This suggests that the titania-containing mesoporous silicas show about 42% higher photo-activity than bulk titania in degradation of oestrogen.

It can be seen that all samples with one loading cycle are less active in photo-degradation of organics. From the results of former chapters, it was proved that there are no titania nano-domains present in these samples. Instead, titania is present as isolated titanium species on the silica surfaces. Especially, S15-D-1, which contains small crystalline anatase titania clusters, is very effective in removing small organic molecules in water. Therefore, this proves that titania nano-domains are more photo-active than isolated titania species. Additionally, from the results of photo-degradation of phenol in water, synthesized titania-containing mesoporous silica (S15-A and S15-B series) can oxidise phenol into by-products, such as p-benzoquinone and hydroquinol, instead of complete oxidation to CO$_2$ and H$_2$O. S15-D-1 was shown to be capable of completely decomposing the organics into CO$_2$. 
and H₂O as shown in Figure 5.5.5, 7 and 8. However, for more bulky oestrogen molecules, S15-D-1 is almost inactive. N₂ sorption measurements show that narrowed mesopores (S15-D-1 are only about 5.2nm, which are smaller that those of S15-B-3, 7.4nm) were blocked or partly blocked. Its low activity can therefore be explained as the blocking mesopores, which limits the access of bulky oestrogen molecules to active anatase titania particles in the mesochannels.

5.5 Conclusions

[A] A multistep impregnation method has been developed. In this method, the self-limiting reaction of titanium tetraisopropoxide (TTIP) with surface hydroxyls in each loading cycle can be fulfilled completely, resulting in the high dispersion of titania in mesoporous silica. Removal of residue TTIP molecules also minimise the growth of titania phase, leaving the growth of titania restricted. XRD, TEM, and N₂ sorption measurements also demonstrate that this method is effective to incorporate high amount titania into the SBA-15 without blocking the mesopores. SBA-15-type mesostructures for both A and B series are quite intact upon incorporation of titania species. No blockage of mesopores were found for S15-A-3 with titania content reaching 24.4wt.%. In comparison, the OSI method leads to the formation of bigger titania particles. Serious blockages of mesopores were acknowledged with regards to the XRD, UV-vis DRS and N₂ sorption measurements.

[B] From the results of Raman and UV-vis-DRS results, very small titania nano-domains up to 1.3nm instead of bulk titania phases were confirmed. N₂-sorption results show that the maintenance of mesopores at the expense of micropores. These titania clusters are proved to be located in the micropores. This explains why the mesopores are free of blockage.
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[C] XPS and FTIR results suggest that, besides the formation Ti-O-Ti phases, Si-O-Ti bonds also exist in the interphases. With the increasing loading of titania, Si-O-Ti bonds increase in quantity but decrease in proportion of Si-O-Ti bonds with regard to the total titania content.

[D] According to the test of photocatalytic performance of titania-containing SBA-15, although the photo-activity on destructing ‘small’ molecules, such as phenol and salicylic acid molecules, is lower than S15-D-1, these materials did show superior photo-activities on photo-destructing oestrogen as compared to S15-D-1. Because the mesopores in S15-D-1 were blocked or partly blocked, the access of ‘big’ oestrogen molecules to active anatase titania particles in the mesochannels was limited. Therefore, the importance of the synthesis of clogging-free TiO$_2$-containing SBA-15 obtained via MSI method is clear.

References


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[34] T. Ohsaka, F. Izumi, Y. Fujiki, J. Raman Spec. 1978, 7, 321


Chapter 6 Conclusions and Future work

6.1 Conclusions

For preparing nickel-containing mesoporous silicas, a modified DS method has been developed in this project. In this method, the connection of nickel ions with TEOS makes the co-hydrolysis and co-condensation possibly occur at molecular level so that the homogeneous dispersion of the Ni in the frameworks of silica can be realized. This allows the incorporation of high amount of nickel into the silica frameworks instead of formation of simple mixture of NiO and siliceous mesoporous silica. In contrast, the unmodified DS method led to the formation of much more extra-framework NiO, while much less into the mesophases.

According to the XRD, TEM, EDX, N2-sorption measurements, via the modified DS method, not only can higher amount of nickel (up to 14.7wt. % Ni) be pretty evenly incorporated into the mesophases but also mesoporous structures are still satisfactory when high amounts of nickel was incorporated. No significant micropores existed in all calcined samples according to the $\alpha_\text{r}$-plots analysis. Especially, mesoporous surface area (more than 840 m$^2$/g) and pore volume (not less than 0.73 cm$^3$/g) can be obtained.

Although sporadic bulk NiO was found, the majority of nickel species existed as nickel strongly interacting with silica, including the formation of nickel phyllosilicates, as elucidated by FTIR, XRD, UV-vis-DRS and XPS results. No Ni$^{3+}$ was found to be present. After reduction at 500 $^\circ$C, nickel clusters around 3nm in size revealed by the TEM measurements, were found to be embedded in the silica walls. Wide-angle XRD confirmed the formation of metallic nickel phases. Although BET surface suffered slight loss, reduced nickel-containing mesoporous silicas showed quite similar low-angle XRD peaks, indicating the preservation of mesostructures after reduction at 500 $^\circ$C. Additionally, mesostructures were found to be intact even upon reduction at higher temperature up to 650 $^\circ$C. Reduction at
650 caused higher reduction degree and growth of metallic Ni particles (around 5nm) bigger than the mesopores. XPS and UV-vis-DRS measurements revealed that the reduction at 500 and 650 destroyed the nickel phyllosilicates and incurred the change in coordination of nickel in mesoporous silica.

✧ For preparing titania-containing mesoporous silicas, a multistep impregnation method has been developed with the aim of incorporation high amounts of titania into SBA-15. In this method, the self-limiting reaction of TTIP with surface hydroxyls in each loading cycle can be fulfilled completely, resulting in the high dispersion of titania in mesoporous silica. Removal of residue TTIP molecules also minimise the growth of titania phase, leaving the growth of titania phase restricted. XRD, TEM, and N2 sorption measurements demonstrated that this method is effective to incorporate high amount titania into the SBA-15 without blocking the mesopores.

✧ SBA-15-type mesostructures for both A and B series are quite intact upon incorporation of titania species. No blockage of mesopores were found for S15-A-3 with titania content reaching 24.4wt.%. In comparison, the OSI method leads to the formation of bigger titania particles. Serious blockages of mesopores were acknowledged according to the XRD, TEM, UV-vis DRS and N2 sorption measurements.

✧ From the Raman and UV-vis-DRS experiments, very small titania nano-domains up to 1.3nm instead of bulk titania phases were confirmed. In S15-A series, titania was more highly dispersed than in S15-B series, because the $\alpha_{OH}$ for the starting pure mesoporous silica SBA-15 for A series was higher than B series. N2-sorption results further showed that the maintenance of mesopores at the expense of micropores. The titania clusters were proved to be located in the micropores. This can explain why the mesopores are free of blockage. XPS and FTIR results
suggested that, besides the formation Ti-O-Ti phases, Si-O-Ti bonds also exists in the interphases. With the increasing loading of titania, Si-O-Ti bonds increase in quantity but decrease in proportion of Si-O-Ti bonds with regard to the total titania content. Additionally, the thermal stability of titania-containing SBA-15s is good. Calcinations at 500, 600 and 700 have no significant influence on the growth of titania phase. Hydrothermal treatment in boiling water led to the breaking of Si-O-Ti and then the formation of bulk titania phase.

According to the test of photocatalytic performance of titania-containing SBA-15, although their photo-activity on destructing ‘small’ molecules, such as phenol and salicylic acid molecules, is lower than S15-D-1, these materials did show superior photo-activities on photo-destructing oestrogen to S15-D-1. Average specific reaction rate normalized by the amount of titania utilized for S15-A-3 S15-B-3 are 1.73x10^{-5}, 1.53x10^{-5}, which is also higher than bulk titania nanoparticles (25nm), 1.20x10^{-5} mol g^{-1} h^{-1}. The titania-containing mesoporous silicas showed about 42% higher photo-activity than bulk titania in degradation of oestrogen. Because the mesopores in S15-D-1 were blocked or partly blocked, the access of ‘big’ oestrogen molecules to active anatase titania particles in the mesochannels was limited. S15-D-1 was almost inactive for destructing such ‘big’ oestrogen molecules. Therefore, the importance of the synthesis of clogging-free TiO_2-containing SBA-15 obtained via MSI method is clear.

6.2 Future work

Based on the current research results, some further work is necessary in the future work. For nickel-containing mesoporous silica:

[A] Study on the reduction process of nickel-containing mesoporous silica is necessary. Firstly, influence of reduction conditions, such as H_2 flow rates, temperatures and heating rates, on the particle size and extent of reduction need to be investigated in great detail using TPR and TEM, etc. H_2 sorption
fraction of incident molecules which actually condense on a surface; $q_1$ is the isosteric heat of adsorption.

For the $\theta_0 = 1 - \theta_1$:

$$\theta_1 = \frac{a_1 kp}{a_1 kp + z_m v_1 e^{-q_1/RT}} \quad (2.3.4)$$

if the $n$ (in moles) is the amount adsorbed on 1 gram of the adsorbent, then $\theta_1 = n / n_m$.

where $n_m$ is the monolayer capacity. According to equation (2.3.4), therefore

$$\frac{n}{n_m} = \frac{Bp}{1 + Bp} \quad (2.3.5)$$

where

$$B = \frac{a_1 k e^{q_1/RT}}{z_m v_1} \quad (2.3.6)$$

Equation (2.3.5) is the familiar Langmuir equation for the case when adsorption is confined to a monolayer. When extended to second layer, the langmuir mechanism requires that the rate of condensation of the molecules from the gas on to molecules already adsorbed in the first layer, shall be equal to the rate of evaporation from the second layer which has been reported by Langmuir the possibility that the evaporation-condensation mechanism can still apply to second and higher molecular layers [2]:

$$z_m \theta_2 v_2 e^{-q_2/RT} = a_2 kp \theta_1 \quad (2.3.7)$$

for the $i$th layer,

$$z_m \theta_i v_i e^{-qi/RT} = a_i kp \theta_{i-1} \quad (2.3.8)$$
Appendix I: BET model

The model implies that at any pressure below the saturation vapour pressure, the fractions of the surface covered with 1, 2 ... i molecules will be \( \theta_1, \theta_2, \ldots, \theta_i \) respectively, so that the thickness of the adsorbed layer will not be constant throughout. On the specific area \( A \), therefore, the total number \( Z \) of molecules adsorbed will be:

\[
Z = Az_m(\theta_1 + 2\theta_2 + \ldots + i\theta_i) \quad (2.3.9)
\]

or

\[
\eta = Az_m(\theta_1 + 2\theta_2 + \ldots + i\theta_i)/L \quad (2.3.10)
\]

Equation (2.3.10) can not be used directly for the different \( q, v \) for different layers. So, Brunauer, Emmett, Teller made three assumptions: (a) that in all layers except the first the heat of adsorption is equal to the molar heat of condensation \( q_L \); (b) that in all layers except the first evaporation-condensation conditions are identical, i.e. that

\[
v_2 = v_3 = \ldots = v_i \quad \text{and} \quad a_2 = a_3 = \ldots = a_i
\]

and (c) that when \( p = p^0 \), the adsorptive condenses to a bulk liquid on the surface of the solid, i.e. that the number of layers becomes infinite (\( p^0 = \) saturation vapor pressure).

These lead to the BET equation:

\[
\frac{n}{n_m} = \frac{c(p/p^0)}{(1 - p/p^0)(1 + (c-1)p/p^0)}
\]

\[
(2.3.11)
\]

or

\[
\frac{p/p^0}{n(1 - p/p^0)} = \frac{1}{n_mc} + \frac{c-1}{n_mc} \frac{p}{p^0}
\]

\[
(2.3.12)
\]
Equation 2.3.12 is the most often used form of BET equation for application to experimental data. Plot of \((p/p^0)/n(1-p/p^0)\) against \(p/p^0\) will lead to a straight line with slope \(s=(c-1)/n_mc\) and intercept \(i=1/\ n_mc\). The solution of these two simultaneous equations gives \(n_m\) and \(c\):

\[
\frac{1}{s+i} = n_m, \quad c = \frac{s}{i} + 1
\]

According to the equation 2.3.2, the total surface area can be calculated by equation 2.3.2:

\[
A = n_m a_m L
\]

References:


Appendix II

List of publications

1) Preparation of high nickel-containing MCM-41-type mesoporous silica via a modified direct synthesis method


2) Multistep Impregnation Method for Incorporation of High Amount of Titania into SBA-15


3) Synthesis and Characterization of high nickel-containing mesoporous silica via a modified direct synthesis method

W Wang, M Song, ZY Zhang and M Richardson, Submitted to Journal of Non-crystalline Solids 2005

4) Synthesis and Characterization of SBA-15 with Titania Clusters Entrapped in Micropores

W Wang and M Song, Submitted to Journal of Non-crystalline Solids 2005

5) Effects of Mesostructures on the Photocatalytic Activities of Titania-containing SBA-15s

W Wang and M Song, Submitted to Applied Catalysis B: Environmental 2005