

CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW
REFERENCE

2.1 Porous Materials

Porous material is the material containing pores, channels, or cavities. Porous materials are divided into three types according to the IUPAC definition: microporous (<2 nm) such as zeolite, mesoporous (2–50 nm), MCM-41, MCM-48 in M41S groups and macroporous (>50 nm), such as porous glasses (Fig. 2.1). Moreover, porous materials may be divided into three types base on the diffraction characteristics: amorphous solids does not give any diffraction peaks, sub-crystal solids give very few broad diffraction peaks or no diffraction peaks, crystal solids give a set of diffraction peaks.

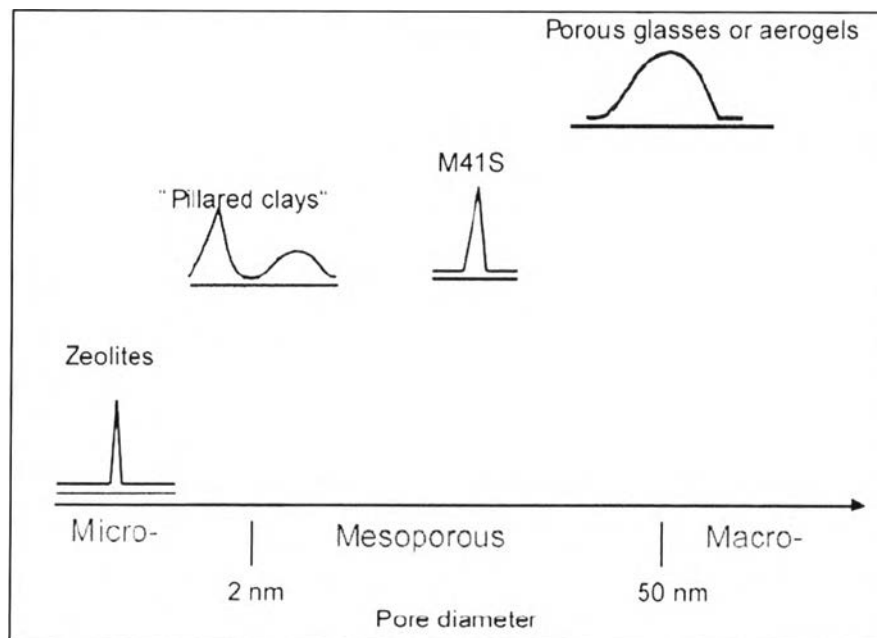


Figure 2.1 Comparison of pore size for porous materials.

(http://www.uio.no/studier/emner/matnat/kjemi/KJM5100/h06/undervisningsmateriale/16KJM5100_2006_porous_e.pdf)

The topology of the pore space of a porous material is very important to determine the properties of the material since it is implied how the pores are connected. If the pores are isolated to each other, it means that the shape and the size of pores are individual pores. Figure 2.2A shows that the pores are random size and unconnected. If the pores are fully connected, as shown in Fig. 2.2B, it means that the pores are fully connected to each other.

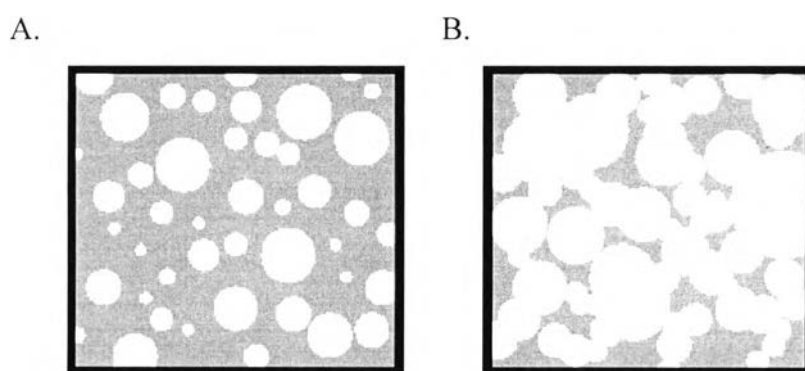


Figure 2.2 Illustration of A) isolated pores, and B) connected pores.
(<http://ciks.cbt.nist.gov/garbocz/appendix3/node2.html>)

The porous materials are extensively used as catalysts, catalyst supports, and adsorbents due to their high surface area and open structure. There are some definitions used to characterize porous materials in Table 2.1.

Table 2.1 The definitions used to characterize porous materials
 (http://www.uio.no/studier/emner/matnat/kjemi/KJM5100/h06/undervisningsmateriale/16KJM5100_2006_porous_e.pdf)

Density	True density	Density of a porous material excluding pores and interparticle void
	Apparent density	Density of a porous material including closed and inaccessible pores
	Bulk density	Density of a porous material including pored and interparticle void
Pore volume	V_p	Volume of the pores
Pore size		Pore width
Porosity		Ratio of the total pore volume to the apparent volume of the particle or powder
Surface area		The accessible area of solid surface per unit mass of material

2.2 Mesoporous Materials

The M41S materials were discovered by scientists from Mobil Corporation. The members of M41S such as MCM-41 (one dimensional, hexagonal ordered), MCM-48 (cubic three dimensional channel structure), and MCM-50 (lamellar two dimensional), in which MCM represents Mobil Composition of Matter. Figure 2.3 shows the structures for M41S mesoporous materials.



Figure 2.3 Structures for M41S mesoporous materials (Carreon *et al.* 2005).

The attractive parts of the mesoporous materials are that they have some outstanding properties which do not have in other porous materials. These properties include:

- (1) Narrow pore size distribution
- (2) High surface area, high porosity, highly ordered pore
- (3) Various structure, wall compositions, and pore shapes

The big advantage of mesoporous material is high surface area and a large pore volume. From these advantages, mesoporous materials provide new opportunities in many applications, such as adsorption, separation, catalyst, sensor and so on.

2.2.1 Synthesis

The core principle to synthesize mesoporous silica is to use surfactant as a template through a sol-gel process. The process is believed to synthesize via the formation of a liquid crystal which is self assembly mechanisms. Size and shape of micelles, hexagonal, cubic, and lamella (Fig. 2.4), into liquid crystals depend on concentration of surfactant and synthetic temperature.

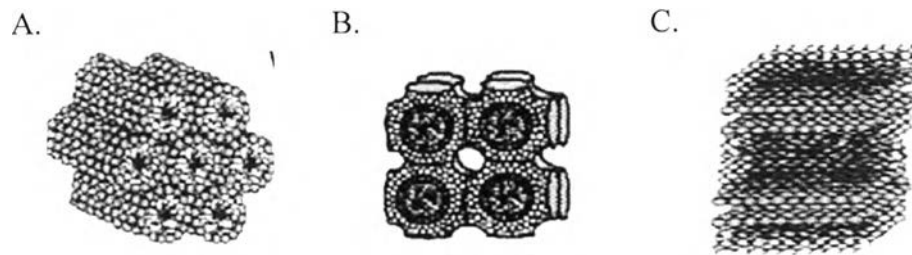


Figure 2.4 Shape of micelle A) Hexagonal, B) Cubic, C) Lamella. (Xu *et al.* 2007)

The mechanism pathways for the formation of mesoporous silica can be described into two pathways: 1) liquid crystal initiated pathway which surfactant molecules are formed to micelle first and then the silicate species are added, 2) silicate anion-initiated pathway which the silicate species and surfactant molecules are associated together to form shapes. Figure 2.5 illustrates mechanism pathways for the formation of MCM-41.

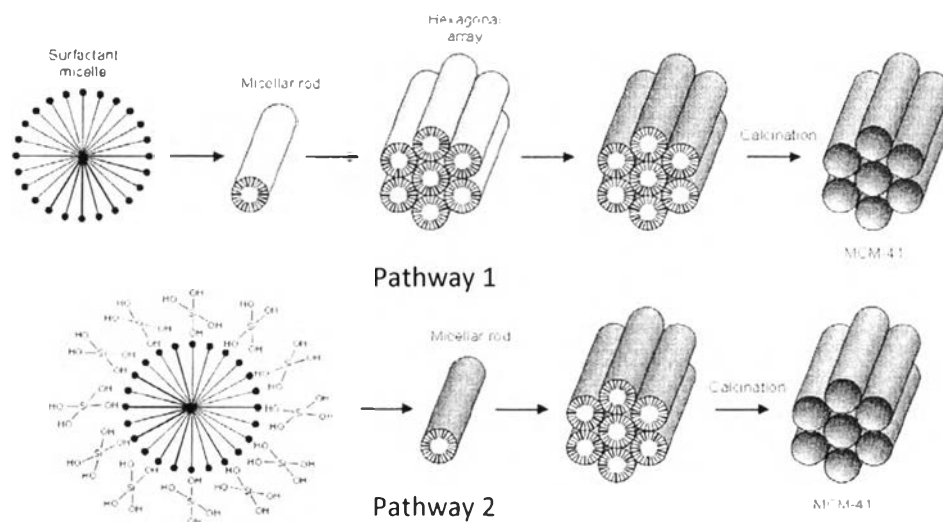


Figure 2.5 Mechanism pathways for the formation of MCM-41.

(http://www.uio.no/studier/emner/matnat/kjemi/KJM5100/h06/undervisningsmateriale/16KJM5100_2006_porous_e.pdf)

2.2.2 Structure of Mesoporous Silica

2.2.2.1 2-D Hexagonal Structure

The 2-D mesostructured materials with hexagonal symmetry and non-interconnected channels include MCM-41 (Fig. 2.6), SBA-3, SBA-15, and FSM-16. The ideal models of structures are hexagonally closed packing cylindrical pore channels which its space group is $p6mm$.

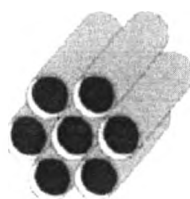


Figure 2.6 2-D mesostructure of MCM-41. (Hui *et al.* 2010)

2.2.2.2 Cubic Channel Mesostructure

Mesoporous silica materials in this group have the 3-D bicontinuous mesochannels like MCM-48 (Fig. 2.7), FDU-5. To date, there are a few of members in the structure family: $la3d$, $Im3m$, and $Pn3m$.

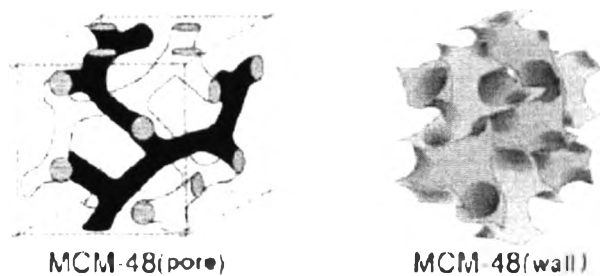


Figure 2.7 The structure of MCM-48. (Hui *et al.* 2010)

2.2.2.3 Caged Mesostructure

This group consists of SBA-1, SBA-6, SBA-12, and FDU-1. Figure 2.8 shows the structure of the caged mesostructure.

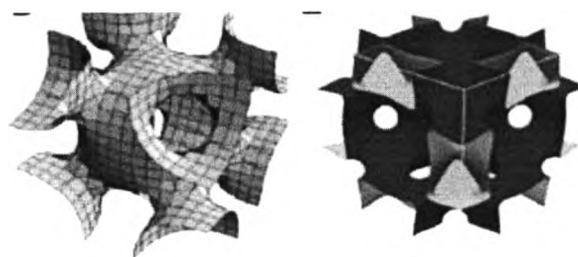


Figure 2.8 The structure of the caged mesostructure. (Hui *et al.* 2010)

The method to synthesize the mesoporous silica was reported by Longloilert *et al.* (2011) The high quality cubic MCM-48 is synthesized via sol gel process using silatrane as a new silica source to replace tetraethylorthosilicate (TEOS) which presents significant handling problems, such as high toxicity and moisture sensitivity. The optimum synthesis condition for synthesizing MCM-48 is as follows; $\text{SiO}_2:0.3\text{CTAB}:0.5\text{NaOH}:62\text{H}_2\text{O}$ at $140\text{ }^\circ\text{C}$ for 16 h. The BET surface area of the MCM-48 is as high as $1300\text{ m}^2/\text{g}$ with a narrow pore-size distribution of 2.86 nm.

2.3 Cerium Oxide

Cerium oxide (CeO_2), also known as ceric oxide, ceria, or cerium dioxide, is one of the most reactive rare earth. Cerium oxide plays an important role in many applications, such as oxygen sensors, solid oxide fuel cells and three-way catalysts for the elimination of toxic auto-exhaust gases. Cerium oxide has two features (Ji *et al.* 2008) which is appropriate for use as catalysts: (1) the oxidation state between Ce^{3+} and Ce^{4+} , $\text{CeO}_2/\text{Ce}_2\text{O}_3$, under oxidizing and reducing conditions and (2) the exhibiting of oxygen storage and release properties, as shown in Fig. 2.9

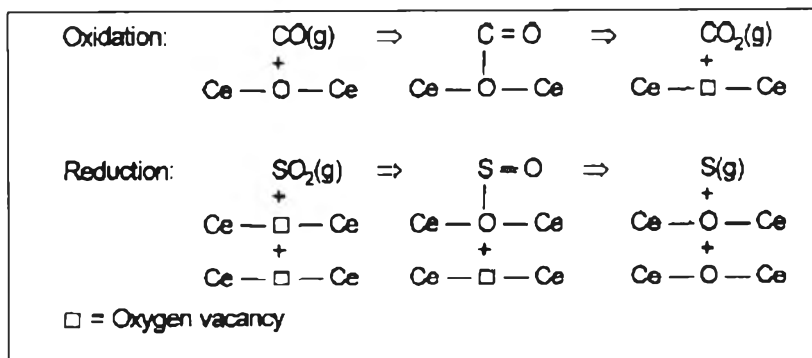


Figure 2.9 The mechanism of CO/SO₂ gas conversion via surface catalysis of CeO₂. (Yu *et al.* 1995)

2.4 Nanocasting

The oldest casting process was to use a liquid material to pour into a cavity mold of the desired shape and then allowed it to solidify. After that, the desired shape solid is ejected out from the cavity mold (Fig. 2.10). Casting method is used for replica the complex shape that is difficult to use other methods. If the casting method reduces scale down to nanometer scale, a suitable word to describe this process is “nanocasting”. Besides the nanoscale, nanocasting transports the fluid or liquid into nanosized void by the capillary condensation while traditional casting uses mechanical infiltration. The first ‘nanocasting’ technique was adopted by Kyotani and coworkers to fabricate microporous carbons using ultra-stable zeolite Y (USY) as a hard template. They fabricated microporous carbons with large surface area (>2000 m²g⁻¹), large microporosity, and high adsorption capacities.



Figure 2.10 Traditional casting process. (Hui *et al.* 2010)

2.4.1 The Nanocasting Process

Nanocasting process involves with nanometer-size pore structure as a mold which is filled with desired material and the mold is removed then replica of the mold is obtained. In nanocasting process, the word ‘mold’ is replaced with the word ‘template’ to avoid any misunderstanding. Basically, templates in nanocasting process can be divided into two kinds; hard templates and soft templates. The first nanocasting was developed from the soft template, such as cationic, anionic, and non-ionic surfactant. The soft templates usually have amorphous or semi-crystalline walls and poor thermal stability. Moreover, it is difficult to control and predict the result of the replica mesostructure due to its much more flexibility and dependence of temperature, solvent, and other parameters whereas the hard templates, such as silica and carbon, are easy to control and predict the result of the mesostructure because the hard templates are fixed.

The nanocasting process (using a hard template) to create nanostructure materials involves in three steps (Fig. 2.11). First, hard templates are infiltrated with a target precursor into the pores. Second, the precursor is converted to the desired material inside the pore by thermal treatment. The last, the hard templates are removed by chemical reaction methods.

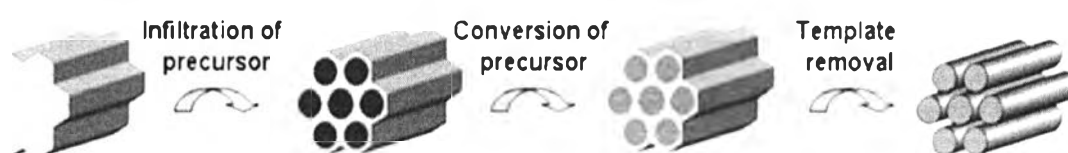


Figure 2.11 Schematic illustration of nanocasting process. (Hui *et al.* 2010)

2.4.2. Hard Templates

One of the hard templates that have been widely used is mesoporous silica due to its various shapes, such as rod like, spherical and fibrous etc. So, the different shapes of replicated mesostructures can be obtained by choosing proper templates. The connectivity of the porous template affects the structure of the porous

replica. When the hard template consists of a fully continuous solid phase and a connected pore channel system, the obtained material can retain a 3-D structure containing framework-confined pores, while the hard template consisting of non-connected pores will produce the replica without framework-confined pores. The important requirement for the hard template is the ability to remove it without affecting the replica.

2.4.2.1 Templates with 2-D Porous Channels

Examples of the hard templates with 2-D channeled mesopore structure are MCM-41, SBA-3, and SBA-15 (Fig. 2.12). The replica of the 2-D porous channel will illustrate nanorods or nanotubes.

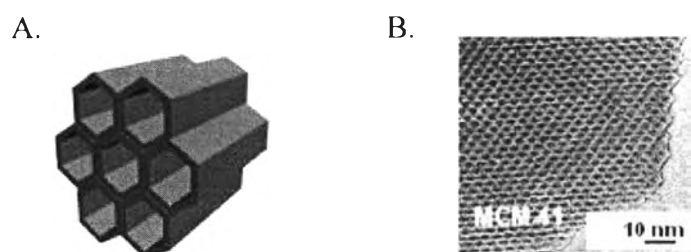


Figure 2.12 Illustrations of A) 2-D porous channel and B) TEM image of MCM-41.
(<http://macs.icgm.fr/spip.php?article21>)

In case of MCM-41 which contains disconnected pores, the replica will show apart rods when removing the template (Fig. 2.13A) whereas SBA-15 which contains interconnected pore system will illustrate ordered nanorods (Fig. 2.13B).

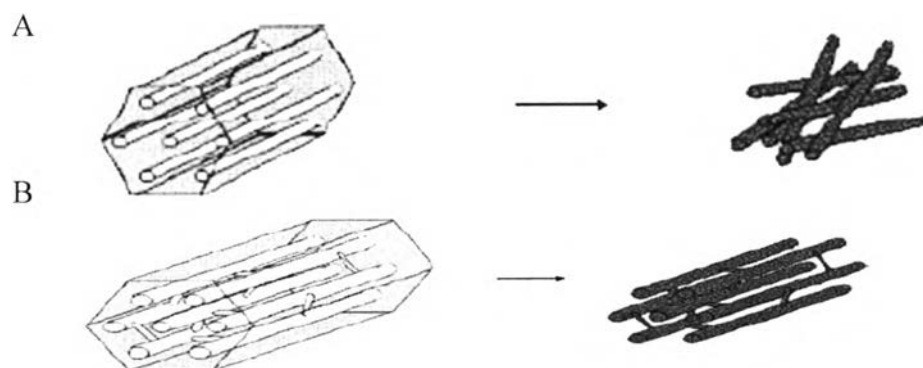


Figure 2.13 Illustrations of A) Disordered nanorods using MCM-41 and B) ordered nanorods using SBA-15. (Hui *et al.* 2010)

2.4.2.2 Templates with 3-D Helix Channels

Mesoporous materials containing 3-D bicontinuous mesochannels are MCM-48, KIT-6, and FDU-5 (Fig. 2.14A). The replica of 3-D helix channel template will illustrate helix nanorods (Fig. 2.14B).

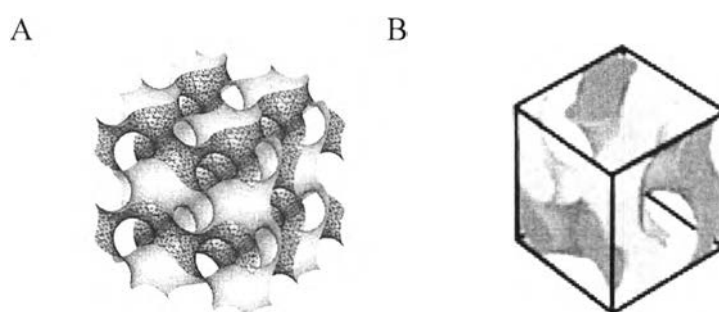


Figure 2.14 Illustrations of A) 3-D helix channels and B) helix nanorods (replica of 3-D helix channels) (http://www.nature.com/nature/journal/v441/n7097/fig_tab/nature04833_F1.html)

2.4.2.3 Templates with Cage-Like Pores

The hard templates with cage like pores include mesoporous silica SBA-1, SBA-16, FDU-1, and FDU-12 (Fig. 2.15). The resulting replicas of the template with cage-like pores are spherical nanoparticles.

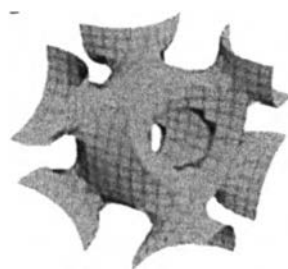


Figure 2.15 Cage-like pores (http://www.nature.com/nature/journal/v442/n7103/fig_tab/442638a_F1.html)

2.4.3 Precursors

The precursors used for the nanocasting process need several requirements. First of all, the precursors should be gaseous, highly soluble or liquid since it must be easily infiltrated and diffused into the pore of the templates. Second, the precursors should be simply converted to the desired materials. Finally, it should not react with the hard template.

The precursor solution can infiltrate to the open pore system by capillary force and their ions are diffused into the vacancies of the template during the evaporation of the solvent. Then, the important factor during the infiltrated step is not only capillary force, but also wettability and mobility of precursors. The amount of precursors that has to infiltrate to hard templates can be calculated from the density of the precursor and the total pore volume of the hard template.

2.4.4 Solvents

Most precursors require a solvent as the carrying medium, thus, solvents are also one of the important factors in nanocasting. The solubility of the precursors is very important for the infiltration. Basically, a high solubility of the precursor provides a better precursor filling and higher infiltration efficiency. Solvents for nanocasting should have low boiling points for easily removing by evaporation. Therefore, ethanol, THF, and water are often used as solvents. Among them, ethanol are usually used in the nanocasting process because of several advantages: (1) it has a lower boiling point and is more volatile; (2) ethanol can dissolve most inorganic precursors; (3) ethanol has a mild interaction with

precursors; (4) ethanol has the amphiphilic property that can be compatible with hydroxyl groups on the surface of the mesoporous silica which improves the capillary force. For the others, water has a strong hydration effect that causes difficulty for the precursor to migrate on the silica surface, and THF has no hydroxyl group and most precursors have low solubility in it.

2.4.5 Method for Removing Templates

The removal of the hard template is the last step to obtain the final nanocast replica. The mesoporous silica template can be removed by using dilute HF solution or hot NaOH solution (at least 2M). HF is very toxic and harmful to human, thus, NaOH is much safer and prefers to be uses for eliminating the silica templates.

The mesoporous carbon template cannot be removed by HF solution or NaOH solution, but can be removed by combustion at elevated temperature in oxygen or air.

2.5 Nanocast Mesoporous Metal Oxides

The hard templates for nanocasting metal oxides always are mesoporous silica which can be removed by HF solution or NaOH solutions. The metal oxides, such as CeO_2 , Cr_2O_3 , Co_3O_4 , Fe_2O_3 , In_2O_3 , and WO_3 , are also used for nanocasting. Some metal oxides which react with HF and NaOH or react with silica template can use carbon template instead.

There are many mesoporous silica hard templates: MCM-41, MCM-48, SBA-15 for nanocast mesoporous metal oxides. The appropriate mesoporous silica should have a suitable pore size for precursors to enter into the pores. Then, MCM-41 with a small pore size and non-interconnected pores is not suitable for nanocast mesoporous metal oxides due to the limitation of diffusion in the small pores and the replicas that cannot keep their structures after the removal of the hard template. Mesoporous silica with high thermal stability is desired to be used as hard templates, such as SBA-15, MCM-48, and KIT-6.

The connectivity of mesoporous silica hard template affects the structure of the mesoporous metal oxide. If the mesoporous silica contains a fully continuous pore, the mesoporous metal oxide obtained will be a 3-D structure that contains

framework confined pores. Moreover, the filling degree of the precursors to the template also affects the structure of the mesoporous metal oxide (Fig. 2.16). Basically, metal nitrates are widely used as precursors since low cost, easy convert to metal oxides, and commercial availability.

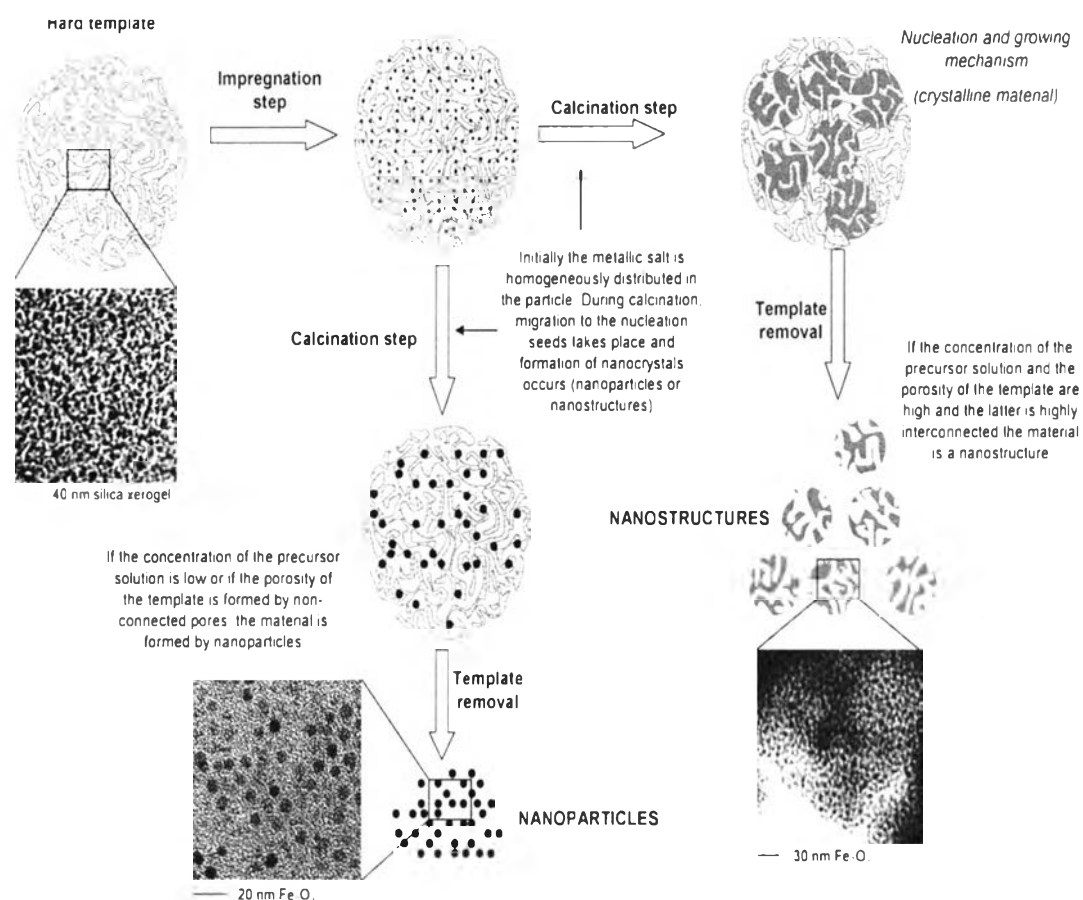


Figure 2.16 Illustration of the nanocasting route (Valdes-Solis *et al.* 2006)

The nanocasting method for CeO₂ synthesized using MCM-48 molecular sieve (with specific BET surface area of 1223 m²/g total pore volume of 1.11 cm³/g) as a hard template was reported by Ji *et al.* (2008). The typical synthesis of crystalline mesoporous CeO₂ was to use Ce(NO₃)₃•6H₂O as a precursor. The cerium precursor/silica composite was subjected to calcinations at 723 K and the process was repeated one more time and calcined again at 873 K, giving the mesostructured cerium oxide with the specific BET surface area of 145 m²/g and total pore volume

of $0.26 \text{ cm}^3/\text{g}$. Ying *et al.* (2011) reported CeO_2 catalysts prepared from MCM-48 hard template via nanocasting process. The CeO_2 loading was 45% by weight. The mesoporous CeO_2 has BET surface area of $222 \text{ m}^2/\text{g}$ and total pore volume of $0.48 \text{ cm}^3/\text{g}$.

Aranda *et al.* (2010) investigated the total oxidation of naphthalene using mesoporous CeO_2 catalysts synthesized by nanocasting from 3D MCM-48 silica templates. The mesoporous CeO_2 was synthesized via nanocasting method by using cerium nitrate as a precursor. The CeO_2 low angle XRD showed a very low intensity peak when compared to the silica employed as a template, suggesting the cerium oxide replicas are less ordered than their silica template. The surface area of CeO_2 obtained was $84 \text{ m}^2/\text{g}$. The results showed that activity of CeO_2 depended on the textural properties of the replica.

Zhang *et al.* (2009) prepared nanocrystalline CeO_2 by nanocasting with mesoporous silica. The cerium nitrate was used as a precursor for mesoporous CeO_2 . The pore size of CeO_2 was about 8.3 nm which is smaller than the pore size of mesoporous silica. Any information about surface area and pore size were not reported.

The influence of cerium salt precursor was studied by Liotta *et al.* (2010). They reported the synthesis of nanosized cerium oxides, starting from cerium nitrate and cerium chloride as precursors and using a high surface area silica xerogels, as template. Four successive impregnations were performed until a final loading of 40% of ceria was used to maximize pore filling and avoid the surface segregation of cerium salt. High surface area was obtained from cerium chloride precursor, exhibiting a surface area as high as $200 \text{ m}^2/\text{g}$ and a small pore size (4.7 nm). Whereas, cerium nitrate provided surface area of $204 \text{ m}^2/\text{g}$ and very small particle size (4.7 nm). SEM images of the ceria obtained from chloride showed a rougher surface than that from nitrate.

Puertolas *et al.* (2010) studied the catalytic performance of mesoporous cerium oxides prepared through a nanocasting route for the total oxidation of naphthalene. The mesoporous silica that was used in this research was a three dimensional *1a3d* cubic mesostructure. The obtained BET surface areas, pore volumes, wall thicknesses, and interconnectivity of the mesoporous cerium oxide are

influenced by the aging temperature during the synthesis of the silica template. The highest mesoporous surface area of mesoporous in this research was 163 m²/g.

Laha *et al.* (2003) synthesized highly thermally stable mesoporous CeO₂ with crystalline walls by bicontinuous cubic structure as hard template. They used inorganic salt CeCl₃•7H₂O as a precursor. The mesoporous cerium oxides had very narrow pore-size distribution. The product with *I* \bar{a} 3*d* symmetry had large surface area and pore volume, reaching to 198 m²/g. and 0.24 cm³/g. The CeO₂ replicas after calcinations at 700 °C showed both mesostructure and crystallinity in spite of a 40% reduction in the BET surface area which indicated that the mesostructure CeO₂ with crystalline wall pores was highly stable upon heating treatment at high temperature.