

CHAPTER II

LITERATURE REVIEW

2.1 Porous Material

Porous material is the material containing pores, channels, or cavities. It can be divided into three main categories, depending on their pore size, according to the IUPAC definition: microporous (<2 nm), such as zeolite, mesoporous (2–50 nm), MCM-41, MCM-48 in M41S group, and macroporous (>50 nm), such as porous glasses, aerogels. Furthermore, depending on the diffraction characteristics of solids, the porous materials may be divided into three types: amorphous, sub-crystal, and crystal. The amorphous solid does not give any diffraction peaks. The sub-crystal gives no diffraction peaks or very few broad diffraction peaks. The crystalline solid provides a set of characteristic diffraction peaks (Xu *et al.*, 2007). Some illustrative porous material examples are given in fig. 2.1.

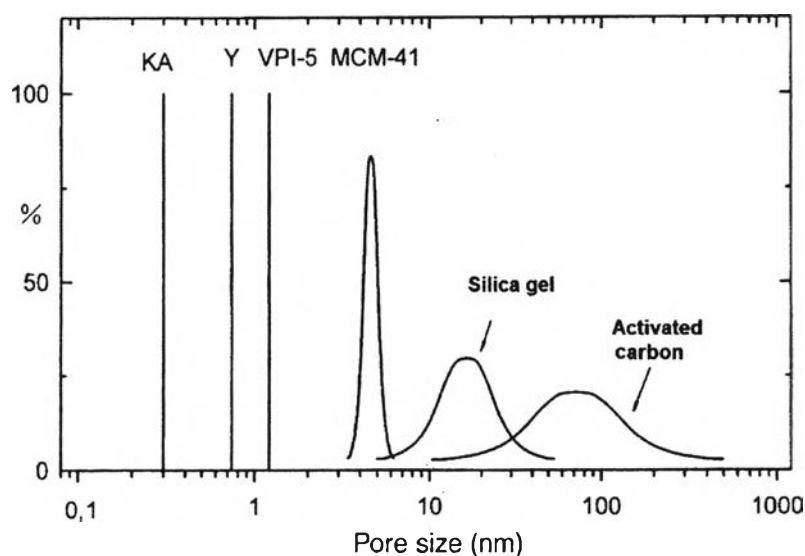


Figure 2.1 Comparison of pore size for typical porous materials (Xu *et al.*, 2007).

The topology of the pore space is a crucial property, regarding flow and transport in porous media. The way how pores are interconnected may be even more

important than their number and size because it is implied how much the pores are connected. The two-dimensional pictures of A) isolated circular pores, and B) connected pores are given in fig. 2.2.

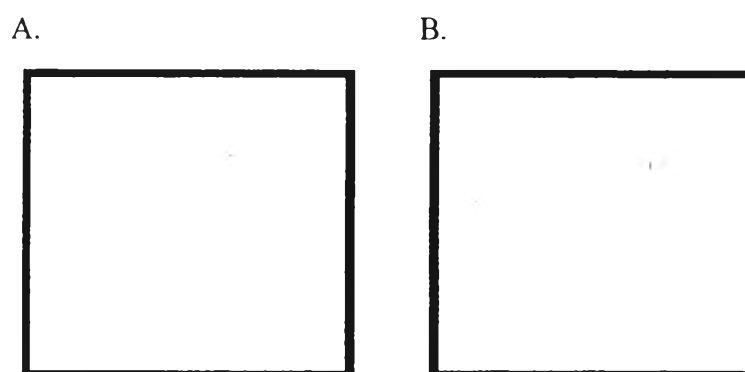


Figure 2.2 The porous materials topology of pore space A) isolated circular pores, and B) connected pores.

The porous materials have been used in various applications, such as water purification, gas separation, catalysts, catalyst supports, electrode materials for energy storage devices, adsorbents, molecular sieve, thermal insulation, etc. (Chaisuwan, T., 2011).

2.1.1 Mesoporous Materials

The ordered mesoporous materials, M41S group (such as, MCM-41, MCM-48 where MCM represents to Mobil Composition of Matter), and SBA-15 are a new generation of materials that are different from nonordered mesoporous materials (Xu *et al.*, 2007). The researchers from Mobil Corporation discovered how to synthesize the M41S materials. The M41S family consists of MCM-41, which has one dimensional hexagonally ordered pore structure, MCM-48, which has three dimensional cubic ordered pore structures, and MCM-50, which has two dimensional unstable lamellar structures. Figure 2.3 shows the structures of M41S mesoporous materials.

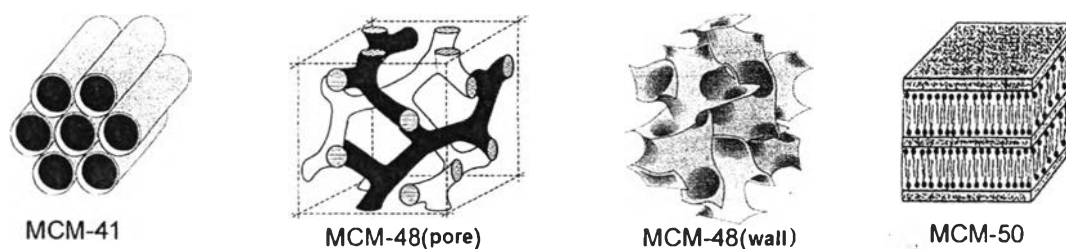


Figure 2.3 The structures for M41S mesoporous materials (Xu *et al.*, 2007).

The ordered mesoporous materials have special outstanding properties that are more attractive than the other porous materials. These properties include:

- (1) High porosity, high surface area, highly ordered pore
- (2) Narrow pore-size distribution
- (3) Various structures, wall compositions, and pore shapes
- (4) Fast diffusion and resistance to pore blocking of coming molecule

The high surface area and a large pore volume are big advantages of the ordered mesoporous materials. From these advantages, mesoporous materials are used in many applications, such as catalysts, separation and adsorption for large organic molecule, and guest-host chemical supporters, etc.

2.1.2 Mesoporous Materials: Synthesis

The most common metal oxide used to synthesize mesoporous materials is silica because silica has a structural flexibility, an ease to control hydrolysis and polymerization of silica species, high thermal stability of silica framework, and an ease to modify the silica surface. The procedure to form the mesoporous silica is from self assembly mechanisms of a surfactant. The surfactant concentration and synthetic temperature are important factors to identify the size and shape (Fig. 2.4) of micelles whether it is hexagonal, cubic, or lamella.

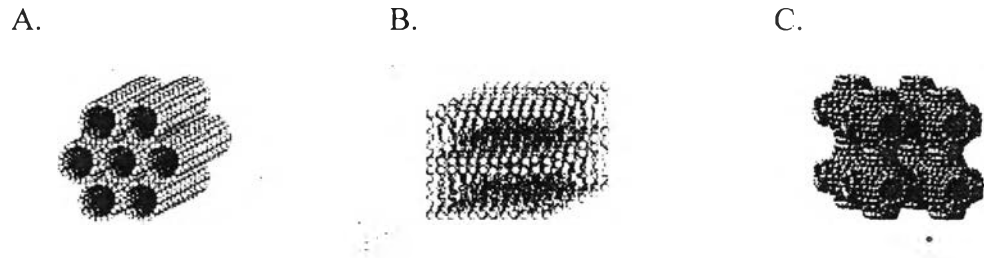


Figure 2.4 Geometric mesostructures of: A.) 2D hexagonal, B.) Lamellar, and C.) Cubic (Juan *et al.*, 2012).

Mesoporous materials exhibit several geometric mesostructures (Lamellar, 2D hexagonal, 3D hexagonal, and cubic), morphologies (powder, nanoparticles, and film), and framework compositions (inorganic organics metal, and metal oxide). There are two mechanism pathways (Fig. 2.5) to form the mesoporous silica: Sol-Gel and self-assembly processes.

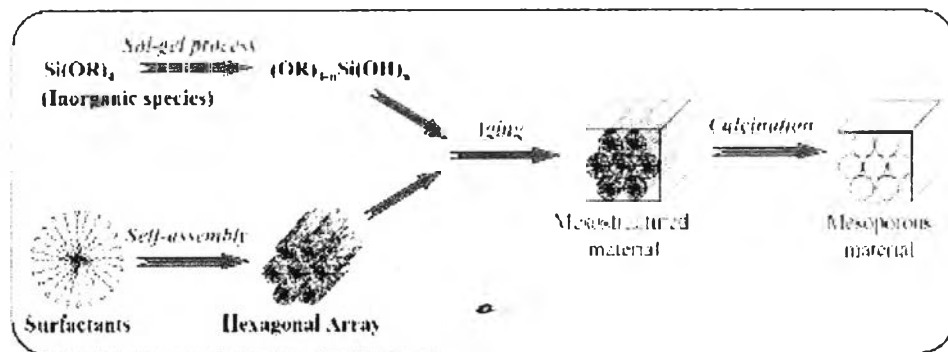


Figure 2.5 Synthesis pathway for formation of mesoporous silica materials (Juan *et al.*, 2012).

Longloilert *et al.* (2011) synthesized mesoporous cubic MCM-48 silica with a high quality via sol gel process using silatrane as a new silica source to replace tetraethylorthosilicate (TEOS) presenting significant handling problem due to its high toxicity and moisture sensitivity. The optimum synthesis condition for synthesizing MCM-48 is $\text{SiO}_2:0.3\text{CTAB}:0.5\text{NaOH}:62\text{H}_2\text{O}$ 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.

2.1.3 Mesoporous Materials: Structure

2.1.3.1 2-D Hexagonal Mesoporous Structure

The 2-D mesostructured materials with hexagonal symmetry are the easiest to produce. There are non-interconnected channels. The classical products compose of MCM-41, FSM-16, SBA-3, and SBA-15. The ideal models of structures are hexagonally closed packing cylindrical pore channels, belonging to the space group is $p6mm$ (Fig. 2.6).

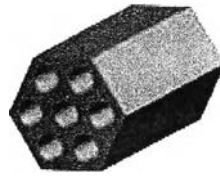


Figure 2.6 The hexagonally symmetric pore arrays (Lu *et al.*, 2009).

2.1.3.2 3-D Cubic Mesoporous Structure

Mesoporous silica materials have the cubic symmetry and 3-D bicontinuous mesochannels. The product in this group composes of MCM-48, KIT-6, and FDU-5, and the model of this family is $Ia3d$ (Fig. 2.7).



Figure 2.7 Pore model of 3-D cubic mesoporous mesostructure with symmetry of $Ia3d$ (Lu *et al.*, 2009).

2.1.3.3 3-D Cage-like Cubic Mesoporous Structure

The product in this group composes of SBA-1, SBA-6, SBA-16, and FDU-12. The models of the structure family are $Pm3n$, $Im3m$, $Fm3m$ (Fig. 2.8).

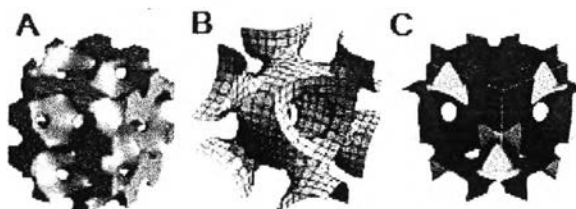


Figure 2.8 Pore model of caged mesostructure with symmetries of A.) $Pm3n$, B.) $Im3m$, and C.) $Fm3m$ (Lu *et al.*, 2009).

2.2 Cerium Oxide

Cerium oxide (CeO_2) is one of the most reactive rare earth metal oxides, which has been widely investigated in the automotive exhaust purification, oxygen storage/release catalyst, and solid oxide fuel cell applications. Cerium oxide is known to play an important role in many catalytic processes; one of those is its use as an additive in the three-way catalyst (TWCs) for automotive exhaust gas treatment (Shen *et al.*, 2005). There are two features which are fitting for making CeO_2 for use as an active catalyst: (1) the redox couple Ce^{3+}/Ce^{4+} , with the ability of ceria to shift between CeO_2 and Ce_2O_3 under oxidizing and reducing conditions, respectively, and (2) the ease of formation of labile oxygen vacancies and the relatively high mobility of bulk oxygen species (Ji *et al.*, 2008).

2.3 Zirconium Oxide

The ZrO_2 ceramics used as advanced structure materials is limited by the spontaneous transformation from tetragonal to monoclinic when from high temperature to room temperature. (Evans. *et al.*, 1986) When the zirconia is blended with some other oxides, the tetragonal and/or cubic phases are stabilized. Effective

dopants include magnesium oxide (MgO), yttrium oxide (Y_2O_3 , yttria), calcium oxide (CaO), and cerium(III) oxide (Ce_2O_3).

2.4 Ceria-Zirconia Mixed Oxide

Ceria-zirconia mixed oxide has potential applications as catalyst support owing to its high surface area, thermal stability, and oxygen storage/release capacity (OSC). Moreover, the present major use of this material is the three-way catalyst promoter. There are many different synthetic methods that are provided to prepare CeO_2 - ZrO_2 and related mixed oxides, including supercritical synthesis, solid state synthesis, co-precipitation, high-energy ball-milling, and sol-gel (Rumruangwong *et al.*, 2008).

Kim *et al.* (2007) studied the characteristics in oxygen storage capacity (OSC) of ceria-zirconia mixed oxides prepared by continuous hydrothermal synthesis in supercritical water. They showed that the continuous hydrothermal synthesis in supercritical water was used as a new synthesis method to obtain ceria-zirconia mixed oxide with better OSC properties. This method has an advantage such that highly crystallized nanoparticles of homogeneous complex metal oxide as well as single metal oxide could be produced easily and rapidly. It was confirmed through physical characterizations with N_2 adsorption, SEM, TPR, and O_2 -uptake that the continuous hydrothermal synthesis in supercritical water could lead to ceria-zirconia mixed oxides with higher thermal stability and better OSC due to its morphology.

Abdollahzadeh-Ghom *et al.* (2011) synthesized mesoporous ceria-zirconia solid solutions via hard template method using KIT-6, SBA-15. The results show that replicas obtained by applying SBA-15 and KIT-6 nanotemplates present similar behavior although KIT-6 shows a slightly higher (about 5%) active surface with values in the range of $125\text{ m}^2/\text{g}$ after thermal annealing and low angle XRD and TEM confirms the mesoporous nature of the oxides.

Kim *et al.* (2012) reported that ceria-zirconia mixed oxides prepared by supercritical synthesis had more potential applications as catalyst support mainly due to its sparsely-agglomerated morphology and higher thermal stability, as compared with those by co-precipitation method (Fig. 2.9).

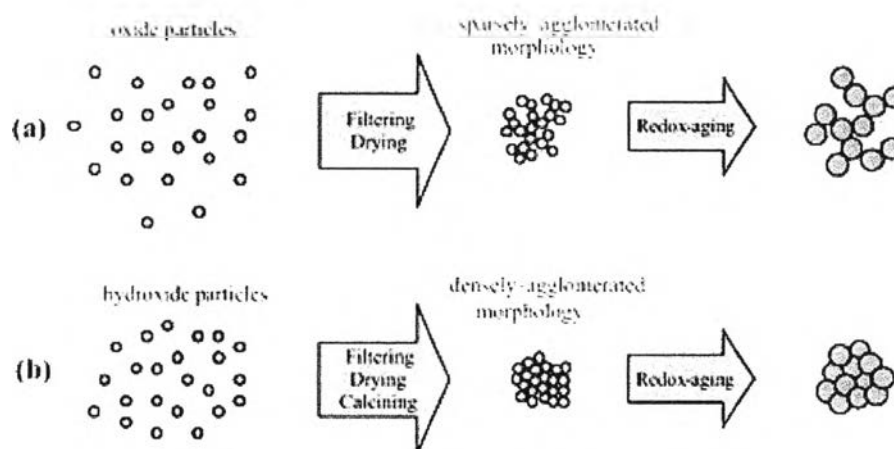


Figure 2.9 Diagram for the changes in the morphologies of ceria-zirconia mixed oxides prepared by (a) supercritical synthesis and (b) co-precipitation method (Kim *et al.* 2012).

The Ce/Zr ratio of the catalyst support was reported by Xu. *et al.* (2012), who reported that the catalyst supported on carrier with 50/50 Ce/Zr ratio behaved the highest catalytic activity because the mesoporous ceria-zirconia solid solution carrier contributed to the activation of CO₂ by its own redox property. The current mesoporous catalyst performed higher catalytic activity and better catalytic stability than catalyst without mesostructure.

As a very important material for exhaust catalysis, ceria-zirconia solid solutions are known to work effectively, benefitting the advantage of large oxygen storage/release capacity (OSC) of ceria due to its the reversible reaction of Ce⁴⁺ to Ce³⁺. However, it lacks high temperature stability, a problem solving by adding zirconium to ceria lattice in order to reduce the electrical resistivity of material (Rumruangwong *et al.*, 2006). Therefore, Ce_{1-x}Zr_xO₂ is known as a promising material for many applications.

2.5 The Casting Process

The old casting process used a liquid or a fluid material to pour into a mold that has a hollow cavity of the desired shape inside and it allowed to be solidified. Then, the solid casting is ejected from the mold (Fig. 2.10). But, this technique is

defined to large size with a limitation in the centimeter range. Therefore, if the casting process is scale down to the nanometer scale, called “nanocasting”. Nanocasting can be used for creating the complex shape in nanoscale that cannot prepare and fabricate by others method.

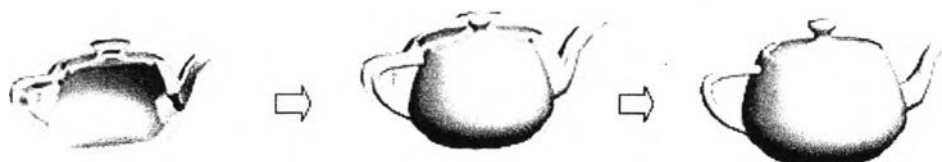


Figure 2.10 The illustration of traditional casting process (Lu *et al.*, 2009).

2.6 The Nanocasting Process

2.6.1 General Principle

The nanocasting process concerns with nanometer size pore structure as a mold (or template) which is filled with the desired material. Then, it is solidified and the template is moved out also the replica of the template is obtained. In the nanocasting process, there are a template that can be divided into two types; (1) soft templates, and (2) hard templates. The soft templates, including cationic, anionic, and non-ionic surfactant, are usually in the molten or liquid state. The soft templates usually have amorphous or semi-crystalline walls and poor thermal stability. Due to its more flexibility and base on temperature, and solvent, resulting in it is hard to control and predict the result of the replica mesoporous. On the other hand, the hard templates, including silica and carbon, are fixed causing it is easy to control and predict the result of the replica mesoporous.

Using a hard template in the nanocasting process in order to create nanostructure materials divide into three steps (Fig. 2.11). First, the precursor infiltrate inside the mesochannel of the template. Second, the precursor is converted to the desired material inside the pore by thermal treatment. Last, the hard template is removed by chemical reaction methods.



Figure 2.11 The illustration of nanocasting pathway (Lu *et al.*, 2009).

2.6.2 Hard Templates

The hard templates have been widely used is mesoporous silica owing to its large internal surface areas and the internal active sites, enhancing shape selectivity, and sorption properties. The connectivity of the porous template directly affects the structure of the solid formed. Then, when the template consists of a fully continuous solid phase and a continuous porous system, the material obtained a 3-D structure containing framework-confined pores. However, hard templates whose porosity is made up of non-connected pores, it will produce solids without framework-confined pores (Valdés-Solis *et al.*, 2006). The ability to remove it without affecting to the replica is the most important necessity for the hard template.

There are three types that can be divided to hard templates. First, templates with 2-D porous channels, including MCM-41, SBA-3, and SBA-15, give nanorods or nanotubes structure. Second, templates with 3-D helix channels (3-D bicontinuous mesochannels), including MCM-48, KIT-6, and FDU-5, provide helix nanorods structure. Last, templates with cage-like pores, including SBA-1, SBA-6, SBA-16, and FDU-12, supply the spherical nanoparticles.

2.6.3 Precursor

The precursor used for the nanocasting process should have some common features. First, the precursor should be able to be easily filled and diffused into the templates, and also should be gaseous, highly soluble or liquid at moderate conditions for easy and sufficient infiltration (Lu *et al.*, 2009). Second, the precursor should be easy to convert to the desired materials. Eventually, the precursor should not react with the hard template. The precursor that contains the solution can first enter the open pore system by capillary force. Then, it is well distributed into all

vacancies of the template and migrated on the surface during the evaporation of the solvent. Moreover, the important factors of precursors not only capillary force, but also wettability and mobility of precursors.

2.6.4 Solvents

Solvents for nanocasting should have low boiling points for easily removing by evaporation. Therefore, ethanol, THF, and water are often used as solvents. High boiling point solvents are not appropriated because it difficult to remove by evaporation.

Ethanol is the best solvent in the nanocasting process because it has many advantages; (1) ethanol has a lower boiling point than water and is more volatile; (2) most inorganic precursors are soluble in ethanol; (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 (Lu *et al.*, 2009). The reason that don't use water as a solvent because it has strong hydration effect results in difficulty for the precursor to migrate on the silica surface, and THF has no hydroxyl group, lower wettability and most precursors have low solubility in it.

2.6.5 Methods for Removing Templates

The removal of the hard template is the final step to get the final nanocast replica. Using dilute HF solution or hot NaOH solution (at least 2M) generally can be removed the mesoporous silica template. Due to HF is the solution that has very toxic and harmful to human. Thus, hot NaOH is more prefer to use than that because it is safer and prefer to be use for eliminating the silica templates.

2.6.6 The Nanocasting Mesoporous Metal Oxides

Mesoporous silica can also be directly used as the mold in the synthesis of mesoporous metal oxides. The silica-metal oxide composite can be prepared by different means, like impregnation by metal salt solutions or dry mixing of the mesoporous silica with precursor salts. The metal oxide/silica composite material is then obtained by thermal precursor decomposition, after which the silica portion is

selectively leached out in either NaOH or HF solutions (Smått *et al.*, 2008). The metal oxides including CeO₂, In₂O₃, MnO_x, NiO, Cr₂O₃, WO₃, Co₃O₄, Fe₂O₃ have been synthesized through the nanocasting technique using mesoporous silica as templates.

- Mesoporous silica used as a hard template for nanocast mesoporous metal oxides includes MCM-41, MCM-48, and SBA-15. The mesoporous silica should have a pore size that the precursors can approach into the pores. However, MCM-41, a small pore size and non-interconnected pore, is not desirable for the nanocast mesoporous metal oxide owing to the small pores make a prohibit of the diffusion and after removal of the hard template, the replicas cannot maintain their structure. Therefore, the mesoporous silica with high thermal stability is desired as a hard template including KIT-6, MCM-48, and SBA-15.

The connectivity of the porous template affects the structure of the solid formed. Thereby, when the template composes of a fully continuous porous system, the material obtained 3-D structure containing framework-confined pores. Essentially, metal nitrate are extensively used as precursor due to low cost, easy conversion metal oxides, and commercial availability.