CHAPTER II
LITERATURE REVIEWS

2.1 Mesoporous Materials

Mesoporous materials, pore sizes of 1.5–40 nm, have been interesting for being used as catalyst and catalyst support because of large surface areas (up to 2500 m^2/g). They are becoming a commercial reality in manufacturing and will continuously grow in the part of efficiency.

A family of ordered mesoporous silicas has the pore size ranging from 2–50 nm. The construction of ordered porous materials is the self-assembly in which molecules spontaneously organize stable well-defined aggregates. These aggregates come from the cationic, anionic, and nonionic surfactants, neutral amines, block copolymers, or their mixtures (Fig. 2.1).
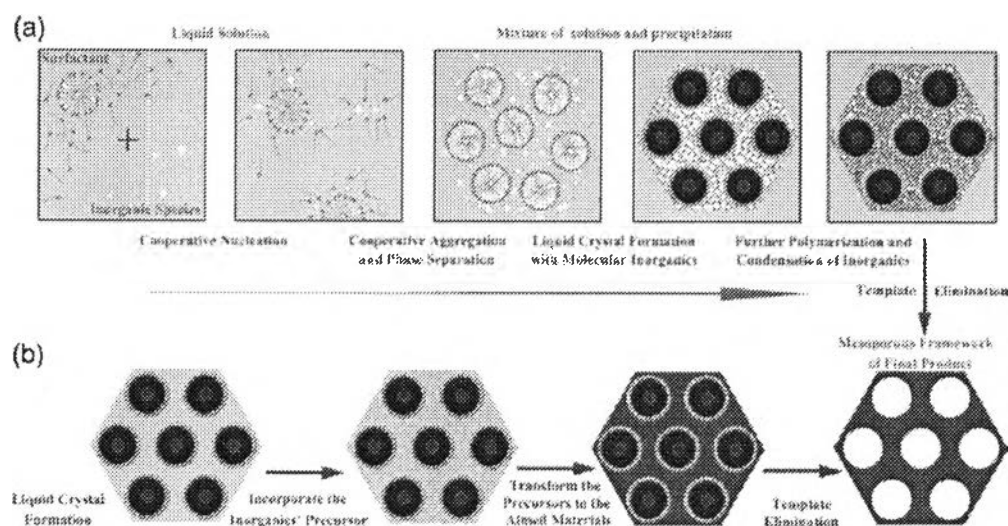

Figure 2.1 Synthetic strategy of mesoporous materials: (a) The cooperative interaction between inorganic and organic species at the molecular scale leads to assembly to 3D ordered arrangements, (b) The true or semiliquid-crystal phase forms 3D ordered arrangements, and then incorporates the inorganic precursors (Jong, 2009).

There are several kinds of different ordered mesoporous silicates having been synthesized and named. Most of the mesostructures belong to hexagonal and

cubic phases. Two-dimensional mesostructured silica, MCM-41, FSM-16, SBA-3, and SBA-15, with the hexagonal symmetry are most easily produced. The ideal model of these structures, having hexagonally close-packed cylindrical pores, belongs to the *p6mm* space group (Fig. 2.2a).
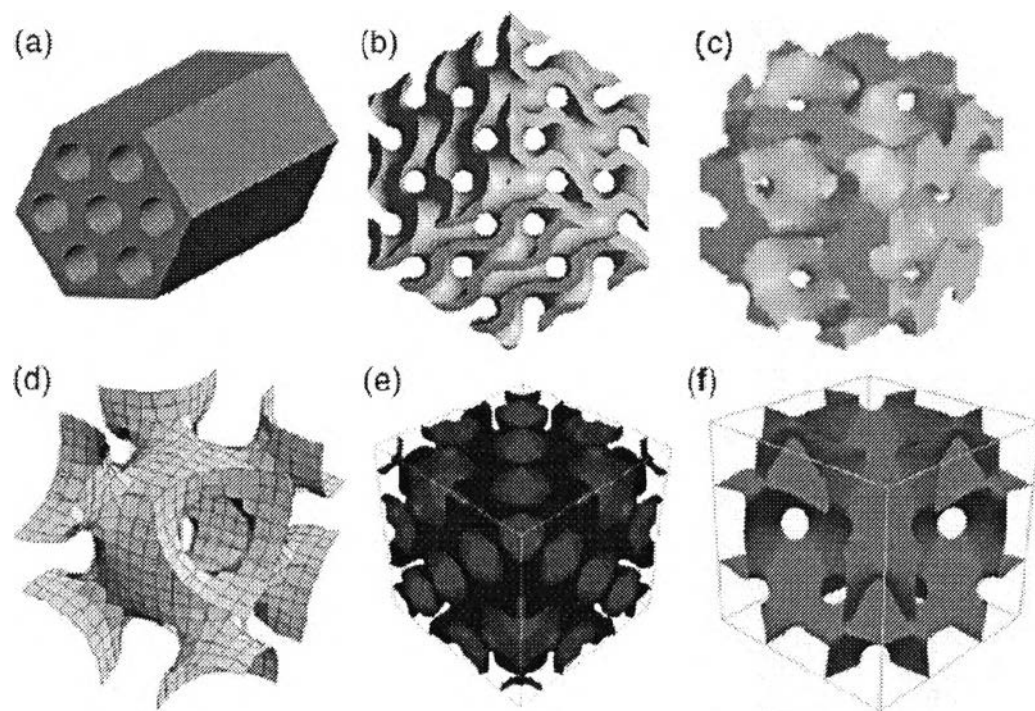

Figure 2.2 Pore models of mesostructures with symmetries of (a) *p6mm*, (b) *Ia3d*, (c) *Pm3n*, (d) *Im3m*, (e) *Fd3m*, and (f) *Fm3m* (Jong, 2009).

The three-dimensional (3D) mesostructures possess the intergrowth of hexagonal close packing (*hcp*) and cubic close-packing (*ccp*) phases, such as, SBA-1, SBA-2, SBA-6, SBA-7, SBA-11, SBA-12, MCM-48, FDU-2, FDU-5, FUD-12, KIT-5, KIT-6, AMS-8 and AMS-10 (Fig. 2.2b-f). Among them, MCM-48 is the extensively investigated mesoporous silica molecular sieves.

MCM-48 is defined by a so-called minimal surface, the gyroid (G-surface). The gyroid surface divides the cube into two identical, but separates compartments, creating two independents, but intertwining enantiomeric 3D pore systems (Fig. 2.3). The 3D structured materials have been interesting over the last years. This can be attributed to the expectation that the 3D pore network could have some important

advantages in catalysis and separation technology, as compared with one-dimensional systems.
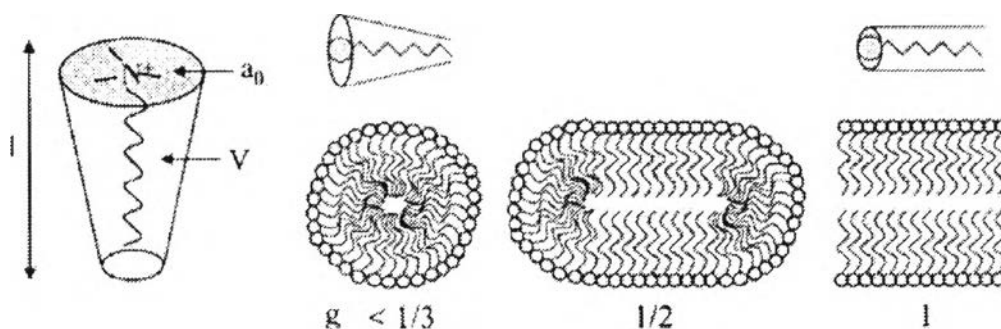

Figure 2.3 The values of the packing parameters systems (Meynen *et al.*, 2009).

The g-factor parameter is widely used for predicting and explaining the final mesostructures. It can be expressed by $g = V/a_0 l$, where V is the total volume of surfactant chains plus any co-solvent or organic additive between the chains, a_0 is the effective hydrophilic head group area at the aqueous-micelle surface, and l is the kinetic surfactant tail length. The expected mesophase as a function of g value is cubic (*Pm3n*) (Fig. 2.4) and 3D hexagonal (*P6₃/mmc*) with $g < 1/3$, 2D hexagonal (*p6mm*) with $1/3 < g < 1/2$, cubic (*Ia3d*) with $1/2 < g < 2/3$, and lamellar with $g \approx 1$.

In the basic synthesis, the cubic *Ia3d* structure becomes favored over the hexagonal one. Therefore, the enhancement of hydrophobic property can easily induce the formation of MCM-48 mesostructure. The characteristics for the synthesis are:
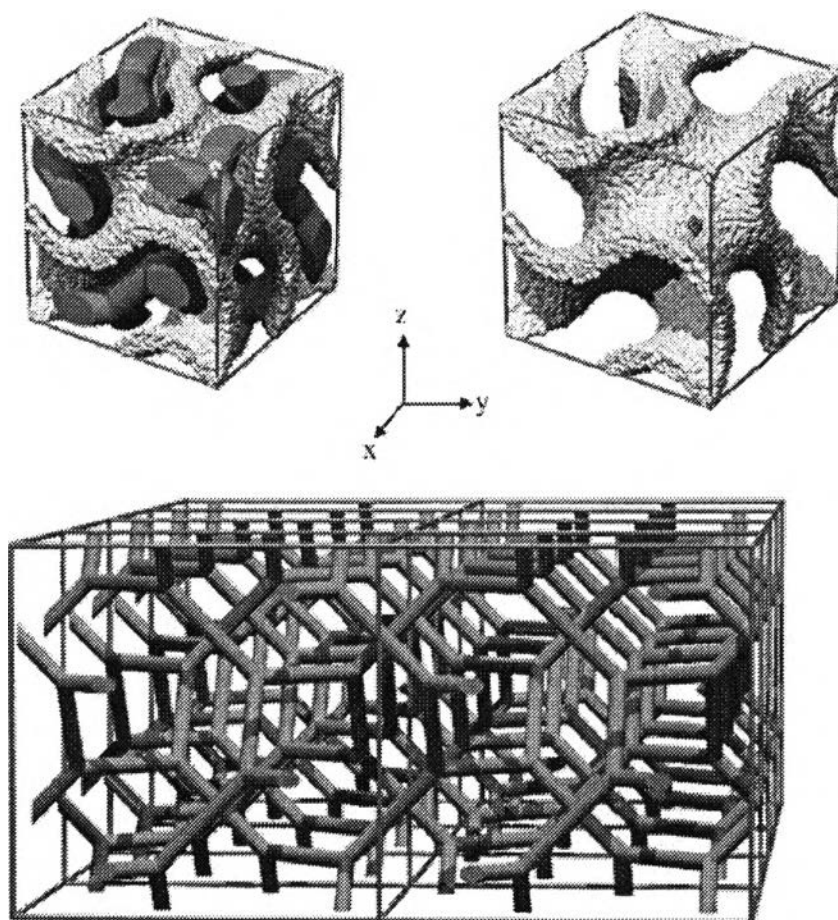
Figure 2.4 Cubic unit cell of MCM-48 with two independent micelle systems (Meynen *et al.*, 2009).

1. Tetraethoxysilane (TEOS) is the best silica precursor in the synthesis of MCM-48. Because it generate ethanol during the hydrolysis, inducing the decrease of the interfacial curvature around the surfactant micelles, thus, resulting in the formation of MCM-48.

2. Moderate polar molecules, such as TEOS, favor the retention of boundary in the hydrophobic zone of surfactant micelles, giving rise to MCM-48 mesostructure.

3. Cetyltrimethylammonium bromide (CTAB) is the most common used as cationic surfactants. Surfactants and large head-group cationic surfactant can easily template the MCM-48 mesostructure.

4. Hydrothermal treatment and recrystallization are needed to improve the mesostructural regularity. (Jong, 2009, Meynen *et al.*, 2009)

2.2 Suzuki Reaction

Biaryl compounds are utilized as important basic skeletons of functional materials, such as liquid crystals and biologically active compounds. Historically, the Ullmann reaction and the Gomberg-Bachmann-Hey reaction have been used for biaryl formation. However, the reaction selectivities and yields of the anticipated products were poor.

In 1981, Suzuki and Miyaura made a breakthrough in the methodology of biaryl compound synthesis by using aryl boronic acids and aryl bromide under homogeneous palladium catalyzed conditions in the presence of bases.

Suzuki-Miyaura reaction (Fig. 2.5) is one of the most popular reactions in modern organic chemistry. It is the coupling of an aryl or vinyl boronic acid with an aryl or vinyl halide and related derivatives (e.g. triflates). The reaction provides a convenient and efficient synthetic methodology for the formation of biaryl compounds or assembly of biaryl systems. (Callam *et al.*, 2001)
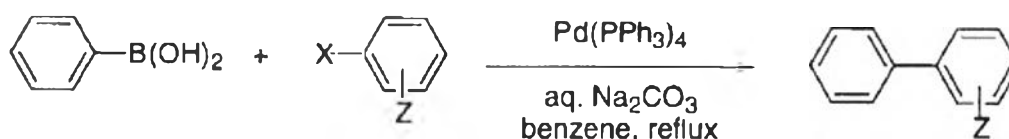

Figure 2.5 Suzuki reaction (Callam *et al.*, 2001).

The cross-coupling reaction proceeds according to a catalytic cycle that involves the oxidative addition of haloarenes or other electrophiles to the palladium(0) complex yielding Ar-Pd(II)-X, transmetallation between pinacol ester of diboronic acid and Ar-Pd(II)-X with the aid of base to gain Ar-Pd(II)-B(OR)$_2$ intermediate. Reductive elimination of arylboronic ester regenerates the palladium (0) complex. The catalytic cycle is shown in Fig. 2.6
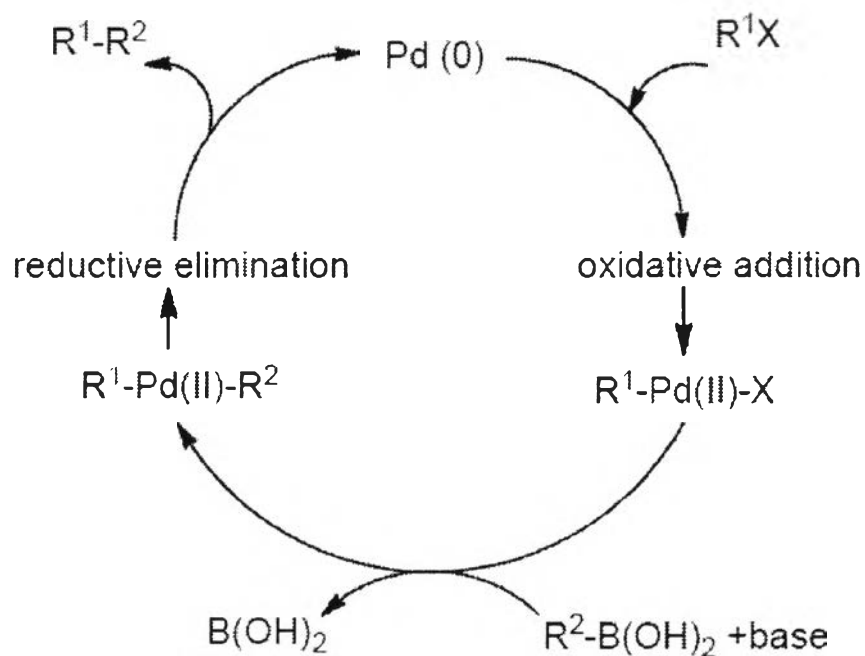
Figure 2.6 Catalytic cycle, the mechanism of the cross-coupling reaction (Lindholm, 2011).

The steps of oxidative addition and reductive elimination are quite well understood, but the transmetallation process is not that well known. There are several processes included in transferring the organic group onto R^1-Pd-X. Bases accelerate the transmetallation between R^1-Pd-X and trialkylboranes or organoboronic acids. However, transmetallation procedure is not the rate-determining step. Organoboron compounds do not react with R^1-Pd-X (X=halogen), but complexes, such as $(RBBu_3)Li$, Ph_4BNa and $(R_3BOMe)Na$, directly undergo a palladium- or nickel-catalyzed coupling reaction.

A variety of homogenous catalysts have also been used, but they are difficult to recover and reuse. Moreover, they could not be used in large-scale synthesis because of environmental and economic reasons, and therefore a reusable and recoverable heterogeneous catalyst is needed.

Supported palladium-phosphines (Fig. 2.7) have been quite attractive catalysts in coupling reactions of arylboronic acids. Silica supported palladium-

phosphines complex is an efficient catalyst for the cross-coupling reaction under mild conditions and it can be reused at least 10 times without loss of catalytic activity. Various organic and inorganic supports have been explored, such as polymers, ionic liquid, charcoal, hydroxyapatite, sepiolite, or other clays, mesoporous silica, and magnetic nanoparticles.
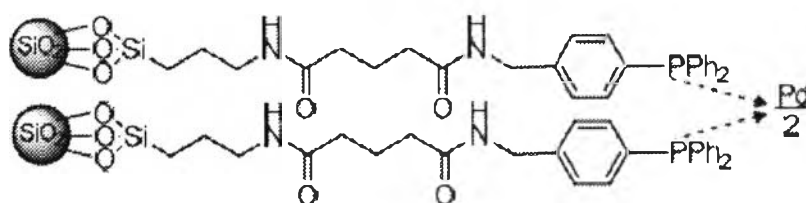

Figure 2.7 Palladium-phosphine catalyst anchored to active silica (Lindholm, 2011).

Generally, the cross-coupling reactions of organoborons and organic halides are carried out in a mixture of an organic solvent and an aqueous solution of base in the presence of palladium phosphine complex catalysts. However, the reaction can also be performed in the presence of ligandless palladium catalyst in water or in water/acetone mixture at room temperature, unfortunately, the catalyst cannot be recovered.

Many metal-catalyzed reactions completely occur in a few min under microwave irradiation. Since polar solvents absorb microwaves, reaction can thus be carried out in water, ethylene glycol (EG), or dimethylformamide (DMF). Microwave irradiation significantly increases the efficiency of ligandless palladium acetate. It can be utilized for both homogeneous and solid-phase coupling reactions of arylboronic acids. For example, the cross-coupling reactions of arylboronic acids and aryl bromides, iodides, and activated chlorides in water are carried out in five min using microwave irradiation to yield phenylbenzene, as shown in Fig. 2.8.
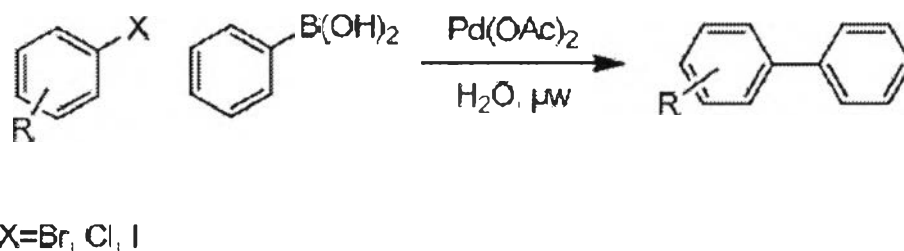
X=Br, Cl, I

Figure 2.8 Suzuki-Miyaura cross-coupling reactions of boronic acids and aryl iodides, bromides and activated chlorides with low palladium loading (0,4 mol %) and reaction time of 5–10 min using microwave irradiation (Lindholm, 2011).

Microwave irradiation is also appropriable for solid-phase coupling reactions. The high temperature reaction may suffer from competitive saponification of the ester group because the main reaction is slow, but the side reaction is retarded by using the microwave irradiation method for less than five min reaction time. (Gradu *et al.*, 2011)

Longloilert *et al.* (2011) reported that silica source named as silatrane was used as a precursor for synthesis of high surface area and high thermal stability of MCM-48 catalyst support. Silatrane was synthesized by mixing 0.1 mol fumed silica, 0.125 mol triethanolamine (TEA), and 100 ml EG whereas MCM-48 was prepared by mixing CTAB, 2 M NaOH solution, and silatrane, using the molar composition of $SiO_2:xCTAB:0.5NaOH:62H_2O$, where $0.15 > x > 0.65$.

Huang *et al.* (2008) synthesized MCM-48 and Al-MCM-48 via hydrothermal approach, using the molar composition of $SiO_2:(0–0.03)Al:0.6NaOH:0.2CTAB:72 H_2O$. In this case, TEOS and aluminum isopropoxide were used as precursors, and the reaction took longer time to provide the desired products.

Chung *et al.* (2012) studied the synthesis methodology of MCM-41and Pd loaded MCM-41 using TEOS as precursor, ammonium hydroxide as catalyst, and CTAB as directing agent. They found that Pd-MCM-41 was an alternative catalyst for manufacturing method of hydrocarbon derived products, such as GBL, THF, and BDO.

Guo *et al.* (2006) found that palladium complexes was a good alternate catalyst to synthesize various fluorinated biphenyl derivatives via Suzuki coupling of aryl bromides and fluorinated phenyl boronic acids in aqueous-phase at room temperature. This approach showed high activity (79-99%), depending on the fluorinated biphenyl derivatives under mild reaction condition, as well as potential recycling of the catalytic species develops environmentally sustainable chemical processes).

Pan *et al.* (2007) successfully developed a highly efficient ligand-free method for the Suzuki coupling between aryl halides and aryl boronic acids using palladium chloride as catalyst. It expressed the excellent yields (> 90%) of the coupling products under mild reaction conditions. Moreover, the palladium could be run four times with synthetically useful results.

Cravotto *et al.* (2005) indicated that biaryls were successfully synthesized using Pd-catalyzed homo- and cross-couplings of boronic acids and aryl halides in aqueous media under high-intensity ultrasound (US) and in dimethyl ether (DME) under microwave irradiation.

Chang *et al.* (2012) reported that Pd/MCM-41 and Pd/SBA-15 were suitable catalysts to microwave-assisted Suzuki reactions under solvent-free condition. The excellent yields of biphenyl were produced from phenyl boronic acid with phenyl iodide and phenyl boronic acid with phenyl bromide using Pd/MCM-41 and Pd/SBA-15, respectively, as catalyst with microwave irradiation for 10 min. However, poor result was shown when the reaction occurred between phenyl boronic acid and phenyl chloride.