

CHAPTER II

LITERATURE REVIEW

2.1 TUD-1 mesoporous material

2.1.1 Synthesis of TUD-1

Mesoporous TUD-1 material has widely been used as catalyst, catalyst support, and adsorbents. The advantage of such material is that it has relatively large pore size, as compared to zeolites, allowing large molecules to diffuse through the pore easily. Thus, TUD-1 is effectively used in the production of fine chemicals and crudes. It is found that TUD-1 can be used not only as a contrast agent in drug delivery system, but also in other potential applications. Because of its advantages, it is worth studying to further improve its applications on various chemical reactions.

Generally, the original synthesis route involves a monomeric silica source of tetraethylorthosilicate (TEOS), mixing with triethanolamine (TEA), and optionally tetraethylammonium hydroxide (TEAOH) since TEA itself can be used as a template for the mesopore formation. Desirable properties of the TUD-1 are: physically stable at high temperatures (200°–250 °C), chemically interacting with the inorganic phase, and inexpensive. The reaction rate increases with pH; to a large extent. This acceleration can also be achieved by increasing the temperature. The second step involves in an aging/drying phase to establish the primary pore structure, and the last step of calcination is required to remove large quantities of organic compounds. However, these methods have several drawbacks from TEOS silica source, such as high toxicity and moisture sensitivity, causing too fast hydrolysis rate. Therefore, silatrane is more interesting silica precursor to synthesize mesoporous materials because of its simple, easy synthesis using low cost starting material (fume silica and TEA) and more importantly, its moisture stability. The synthesized TUD-1 is characterized using X-ray diffractometer (XRD), N₂ adsorption–desorption isotherms, and electron microscopy. Figure 2.1 shows typical XRD pattern and TEM image of TUD-1. Unlike other mesoporous materials, XRD of TUD-1 has not only a broad peak at low 2θ, but also a broad background peak of

amorphous phase. The TEM shows that the pores with diameter of about 5 nm have no apparent periodicity.

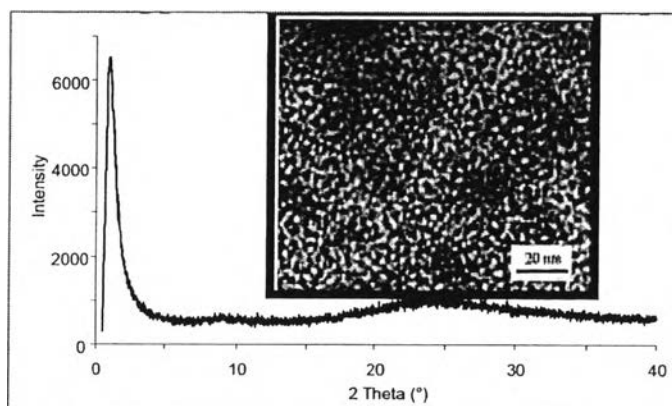


Figure 2.1 Typical XRD pattern and TEM image of TUD-1 (Angevine, *et al.*, 2008).

TUD-1 also holds the narrow pore size distribution, as illustrated in Fig. 2.2, giving only one single peak derived from the nitrogen desorption isotherm. Moreover, an important feature of the material is the easy tunability of the pore sizes over a wide range while maintaining a narrow pore size distribution.

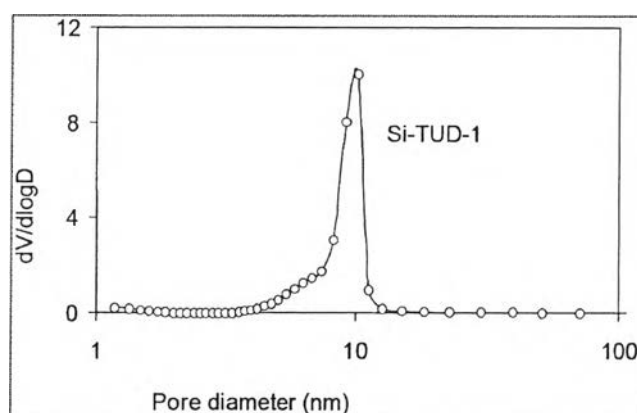


Figure 2.2 Typical pore size distribution of TUD-1 (Angevine, *et al.*, 2008).

One of the methods to synthesize TUD-1 is called sol-gel process. This technique has obtained much attention in materials research in the recent years due to its unique advantages, such as low temperature processing, high uniformity of

final products, and its capability of generating materials with controlled surface properties, and pore structures between 1 and 500 nm. Silica polymers obtained by the sol-gel process undergo hydrolysis followed by condensation reactions. The process generally starts from silicon alkoxide precursor, such as TEOS. By controlling synthesis conditions, the sol morphology can be directed to weakly-branched polymeric systems or to particulate systems (Brinker, *et al.* 1990). Important processing parameters are water content, solvent, catalyst used, concentration, and type of alkoxide used (de Lange, *et al.* 1995). It is important that the effects of these parameters become well-considered in the sol-gel method, a reliable and practical technology, for industrial applications (Fardad, *et al.* 1995).

Charoenpinijkarn *et al.* (2001) explored that the silatrane complexes were a family of organosilicate compounds derived from the reaction of SiO₂ with trialkanolamines, such as TEA or triisopropanolamine. These silatrane complexes are hydrolytically stable in the air up to several weeks. For this reason, they are good candidates for use as precursors in ceramic processing via the sol-gel technique.

Zhang *et al.* (2006) reported the synthesis of mesoporous alumina TUD-1 with high thermal stability via the sol-gel process using tetraethylene glycol (TEG) as a template and studied the effects of TEG and mixed solvents between ethanol and isopropanol on the pore structure of the final products. They found that TUD-1 had amorphous framework, high surface area, large pore volume, and narrow pore size distribution, causing TUD-1 to have high thermal stability upon prolonged heat treatment at high temperatures. These properties are essential for applications in adsorption and catalysis. When the amount of TEG increased, the pore size and the pore volume increased. The mixed solvents also played the role of pore-forming agents in the absence of TEG, but had no obviously directing effect on the structure of mesopore in the presence of TEG.

2.1.2 Synthesis of Metal loaded on TUD-1

There are several preparation procedures currently available that can disperse a metal precursor into contact with the support. Most common one is impregnation, normally used in manufacturing industry for practical and economic reasons. Impregnation can be done via two methods, i.e., wet and dry impregnations.

The dry impregnation, also referred as pore volume impregnation, uses little solution of precursors to fill the pore volume of the support. The solubility of the catalyst precursors and the pore volume of the support are used to determine the maximum loading available for each time of the impregnation. Several successive impregnations and heat treatments may be necessary if high loading is required. On the other hand, the wet impregnation dips the support into excess of the solution, comprising the precursors of the active phase. So, this technique can be called Impregnation in Excess of Solution (IES). In this project, the wet impregnation technique was applied to synthesize Pd-TUD-1.

In general, impregnation primarily consists of three processes: transport of solute to the pore system of the support bodies, diffusion of solute within the pore system, and uptake of solute by the pore wall. In addition, the wet impregnation requires the operation of the fourth process which is the transport of solute to the outer particle surface. In this process, different profiles of the precursors of the active phase over the support body will be resulted from different process conditions. For example, the interaction with the support based on the pH can be either strong or weak, or even repulsion can occur (Mul, *et al.* 2005).

Wang *et al.* (2011) showed that thin nitrogen containing carbon (NC) layer can be coated on the surface of porous silica TUD-1 by carbonizing adsorbed polyaniline as a palladium catalyst support for oxidation of benzyl alcohol. The authors also loaded the Pd nanoparticles on different catalyst supports using wet impregnation method. In a typical synthesis, 1g of TUD-1 support was suspended in 10mL of deionized water with stirring, followed by adding 10 mL of aqueous Pd(NO₃)₂ solution. The amount of Pd loading was kept at 1 wt%. The mixture was then stirred for 18 h to allow the adsorption of Pd precursor on the carbon surface. Subsequently, the water was evaporated while stirring at 80 °C. The resulting solid powder was calcined in Argon at 250 °C for 30 min and reduced in H₂ at 400 °C for another 30 min.

2.2 Metal loaded mesoporous materials and its applications

2.2.1 Suzuki-Miyaura coupling reaction

Generally, the aim of transition metal-catalysed organic synthesis is to form the carbon-carbon (C-C) bond. In this manner (Fig. 2.3), the Pd-catalysed Suzuki-Miyaura coupling reaction, or Suzuki cross-coupling reaction (Miyaura, *et al.* 1981), is one of the most efficient methods for the formation of C-C bonds (Kosslick *et al.* 2001). The palladium Suzuki cross-coupling reaction is an efficient synthetic route to biaryls compounds which play an important role in numerous applications in pharmaceuticals, polymers, advanced materials, and liquid crystal (Gürbüz, *et al.* 2010). Suzuki cross-coupling reaction is usually begun with aryl iodides, bromides, or chlorides to react with phenylboronic acid under palladium metal catalyst in the presence of suitable bases (Fig. 2.4). Suzuki cross-coupling reaction is endowed with mild reaction conditions or nontoxic conditions, commercial availability of the other organometallic reagent, and the ease of being done by basic method, such as microwave irradiation (Wang, *et al.* 2011). The advantages of this reaction are the ease to be processed and separated the product or catalyst. Due to its advantages, Suzuki reaction has thus been used in many industrial applications.

In addition, Suzuki coupling is a palladium-catalyzed cross-coupling reaction. That is, the two molecules are assembled on the metal-carbon bonds in which the carbon atoms and palladium are bound closely together, and, then, are coupled to each other, resulting in a new carbon-carbon single bond.

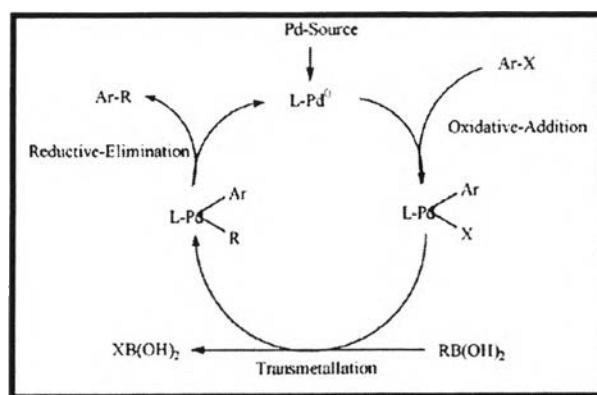


Figure 2.3 General mechanism for the Suzuki cross-coupling reactions (Joshaghanin *et al.*, 2007).

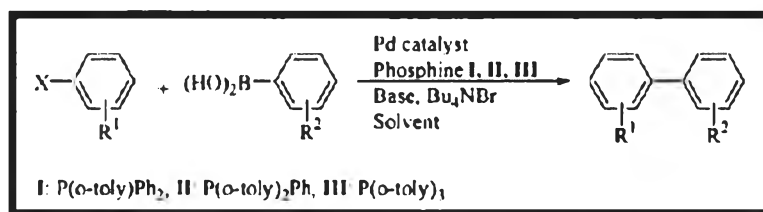


Figure 2.4 Screening the reaction of aryl halides with arylboronic acid (Joshaghanin, *et al.*, 2007).

Miyaura *et al.* (1981) reported the palladium-catalyzed cross-coupling reaction of phenylboronic acid with haloarenes in the presence of bases to give good yields of products. They began to examine the effect of reagents, bases, and reaction conditions on the yield of biphenyl in the reaction of phenylboronic acid with halo-benzenes using benzene as a solvent and 3 mole % of Pd(PPh₃)₄ as a catalyst.

2.2.2 Porous materials used in Suzuki-Miyaura coupling reaction

Kosslick *et al.* (2001) illustrated the Suzuki reaction over palladium-complex loaded on MCM-41 catalysts. The PdCl₂[Ph₂P(CH₂)₂S(CH₂)₃SO₃Na]₂ complex was used as a catalytically active precursor and was directly loaded onto mesoporous catalyst supports. This mesoporous catalyst support was prepared by anchoring the alkylsilylsulfonic acid to the calcined Al-MCM-41. The catalytic tests were then performed in a batch reactor at 78 °C in a toluene/ethanol/water mixture with sodium carbonate as base and CTAB as surfactant. The results indicated that Pd-complex/MCM-41 catalysts were successfully used in the Suzuki C-C-coupling reaction. Moreover, the catalysts were also recycled and re-used.

Gürbüz *et al.* (2010) prepared palladium (II)-containing siliceous-MCM-41 by the reaction of silica precursors (imeo) and MCM-41. They found that the catalyst could be used in the Suzuki reaction of aryl chlorides and phenyl boronic acid. The lower amount of coke formation due to the unique mesoporous structures played a crucial role in the high activity on the mesoporous catalyst. In addition, Pd-MCM-41 showed higher activity than single metal catalyst and the highly dispersed palladium on the mesoporous structure provided more active sites for the complete conversion on the mesoporous catalyst. Thus, the supported mesoporous catalysts are

very useful in developing catalysts for complete coupling reactions and avoiding the problems associated with the side product which caused by deboronation of boronic acid substrates during the reaction process.

2.2.2 Microwave-assisted Suzuki-Miyaura coupling reaction

In organic chemistry, the use of microwave has become increasingly popular, due to the availability of commercial microwave equipment and the short reaction time (Lidström, *et al.* 2001). Generally, thermally driven organic transformations occur by two approaches, i.e., conventional or microwave accelerated heating. In the former approach, a conventional external heat source slowly activates reactant by passing first through the walls of the vessel before going to the reactants. This is a slow and inefficient method for transferring energy into the reacting system. On the other hand, the microwave accelerated heating approach allows microwave irradiation to directly go through the molecules of entire reaction mixture, leading to a fast increase in temperature (Mul, *et al.* 2005).

Leadbeater *et al.* (2003) showed that the reaction of activated aryl bromide with an arylboronic acid in water, using tetrabutylammonium bromide (TBAB) as a phase-transfer catalyst, results in a successfully coupled biaryl Suzuki product without the aid of a palladium catalyst (Fig. 2.5).

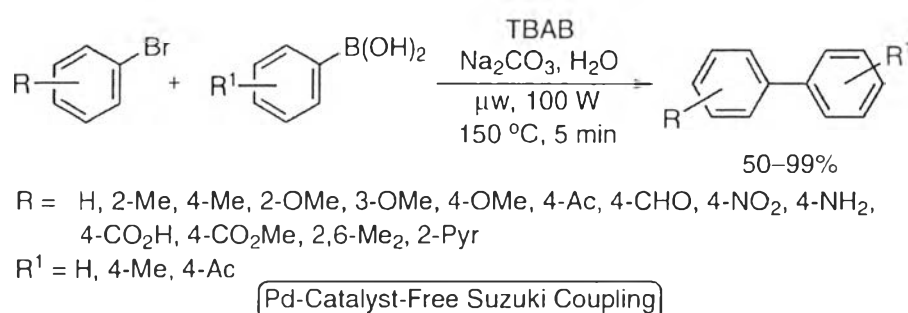


Figure 2.5 The reaction of aryl bromide with aryl boronic acid (Leadbeater, *et al.*, 2003).

McDaniel *et al.* (2011) worked on the Suzuki–Miyaura cross-coupling of benzylic bromides under microwave conditions. They provided a protocol for achieving benzylic Suzuki coupling with moderate to good yields, and also studied

the experimental conditions to improve the yield of their products. Several modifications were explored in this paper, showing that increasing the time or the temperature did not improve the yield. The use of DMF as a solvent slightly increased the yield, as compared with the use of dioxane and THF. Moreover, changing type of base had no effect on the yield either. Studying the type of Pd catalyst, McDaniel *et al.* found that the use of PdCl₂ had no effect on the yield. In addition, several bulky electron-rich Buchwald phosphine ligands such as SPhos, JohnPhos and Cyclo JohnPhos (Fig 2.6) were chosen since the use of these phosphine ligands and Pd(OAc)₂ as the catalysts resulted in the greatest increase of the yield. These ligands were then shown to accelerate the oxidative addition and reductive elimination processes due to their bulky electron-rich phosphine groups. In conclusion, the authors found the optimum conditions for the Suzuki reaction to give a highest yield where Pd(OAc)₂ was used as the catalyst and JohnPhos was used as the phosphine ligand, potassium carbonate as base, and DMF as the solvent.

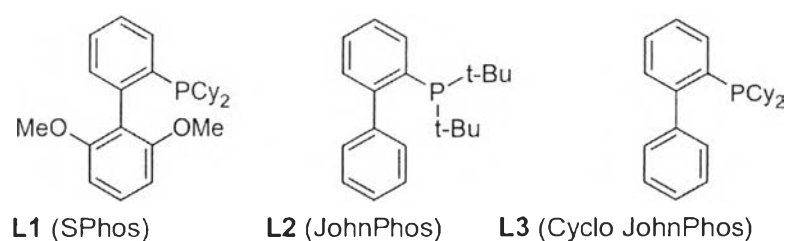


Figure 2.6 Buchwald phosphine ligands.

Chang *et al.* (2012) reported the efficient microwave-assisted Suzuki reaction using Pd/MCM-41 and Pd/SBA-15 catalysts, prepared by impregnation of [Pd(NH₃)₄]Cl₂ on MCM-41 and SBA-15, respectively, in solvent-free condition. The reaction, consisting of phenyl boronic acid, phenyl bromide, K₂CO₃, and Pd-catalyst, gave excellent yields of biphenyl product.

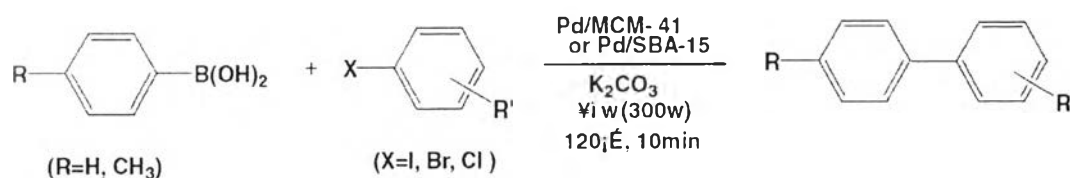


Figure 2.7 The microwave-assisted Suzuki reaction by Chang *et al.* (2012).