



CHAPTER II LITERATURE REVIEW

2.1 Poly(vinyl alcohol) (PVA)

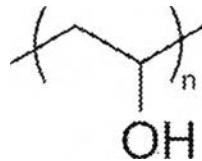


Figure 2.1 Molecular structure of PVA.

Poly(vinyl alcohol) is a hydrophilic polymer which is also water-soluble due to hydroxyl side groups along the polymer chains shown in figure 2.1; hence, it absorbs water and swells easily, but swelling behavior can be inhibited by adding salts (Li *et al.*, 2008). Koski. *et al.* suggested that, the dissolution of PVA varies due to type of solvent, temperature, and degree of hydrolysis. In Aqueous phase, water, there is hydrogen bonding between inter- and intramolecular chains, among hydroxyl groups on PVA themselves and hydroxyl groups on PVA with hydroxyl groups of water molecules. Therefore, to overcome such attractive force which might cause gel formation, heating over 80 °C is necessary. Moreover, chemical and physical properties of PVA depend on degree of hydrolysis because water acts as a plasticizer, more water absorbed causes higher elongation and flexibility, whereas tensile strength is reduced. The preparation of PVA is via hydrolysis of poly(vinyl acetate) partially or completely in order to remove acetate groups from the polymer chains

In industries, PVA is widely used as adhesive or thickener in latex paints, glue, paper coating and even shampoo. PVA doesn't stick on epoxy; therefore, PVA is usually used as a mold-release agent in composite fields. PVA is also used as a lubricant in hard contact lens solution and eye drops. PVA has good chemical resistant, film forming ability, and processibility. Moreover, PVA is biocompatible, non toxic, odorless, and moisture and air permeable. According to such specific properties, PVA has been reported of being applied in medical and healthcare applications; such as wound dressing material, controlled-drug release material, and scaffolds.

Li *et al.* (2008) have reported that in fabrication of PVA via electrospinning technique, adding salts promoted smoother and thinner jet. The addition of ionic salt improves jet surface charge density and jet conductivity. It is considered that the solution with a higher amount of LiCl has a higher net surface charge density. As jet conductivity increased, higher elongation forces are imposed to the jet under the electrical field. Thus smooth and thin jet was obtained when electrospun PVA solutions with the addition of LiCl. The addition of the salt was found to be relatively more effective on the fiber diameter than other parameters.

There have been many researches focused on electrospun PVA recently. Most studies involve incorporating the second component into PVA solution and directly fabricate nanofiber by electrospinning since the electrospinning process is cheap and simple. Jin *et al.* (2007) have successfully prepared PVA containing silver nanoparticles for anti-microbial applications using electrospinning technique. Two pathways were reported. Firstly, they applied AgNO₃ in 12% PVA solution and refluxed the mixture at various temperatures, 50-80 °C and then directly electrospun the solution. Secondly, they electrospun PVA/AgNO₃ and annealed the as-spun fibers, the silver ions remained in the fiber were reduced during annealing process.

Kenawy *et al.* (2007) developed PVA nanofibers for controlled drug release system of Ketoprofen as non-steroidal anti-inflammatory drug (NSAID) using both fully hydrolyzed and partially hydrolyzed PVA electrospun fibers to encapsulate the particular drug. It was found that Fully hydrolyzed PVA can be stabilized against disintegration in water and its visual mechanical properties was improved by treatment with lower alcohol such as methanol.

Recently in 2007, fabrication of PVA/chitosan blend nanofibers produced by electrospinning was reported. Jia *et al.* discovered that fiber morphology and diameter can be affected by concentration of the blend solution and weight ratio of the blend. Strong hydrogen bonding took place between PVA and chitosan molecules. PVA and chitosan were dissolved in water in different containers and two systems were mixed together at different weight ratio before the solution was subjected to electrospinning apparatus.

2.2 Electrospinning

Electrospinning is a simple technique for producing micro- and nanofibers of organic polymers and inorganic oxide materials. It has potential application in filters, tissue engineering scaffolds, wound dressings, drug delivery materials, biomimetic materials, and composite reinforcement, etc. A review by Huang *et al.* (2003) shows a phenomenal increase in the number of publications on electrospinning in recent years. Since electrospun fibers find application in both nanotechnology and biotechnology, this certainly can be seen as a driving force behind the recent renewed interest in a technique that has been known since the 1930's.

The principle behind electrospinning is relatively simple: A solution of a polymer flows out of the tip of a capillary, where a droplet forms under the influence of the surface tension of the solution. A sufficiently large electric voltage (C5–25 kV DC) is applied to the solution, which causes repulsive electrostatic forces between polymer and solvent molecules to overcome the surface tension, and a jet of polymer shoots away from the capillary towards a grounded collector as illustrated in figure 2.2. In the space between the capillary tip and the collector, the jet becomes unstable and a rapid whipping of the jet follows. This leads to evaporation of the solvent, leaving a polymer fiber, which undergoes stretching and thinning as a result of the whipping, and finally collects on the grounded collector as a randomly oriented web of micro or nanofibers. (Smit *et al.*, 2005)

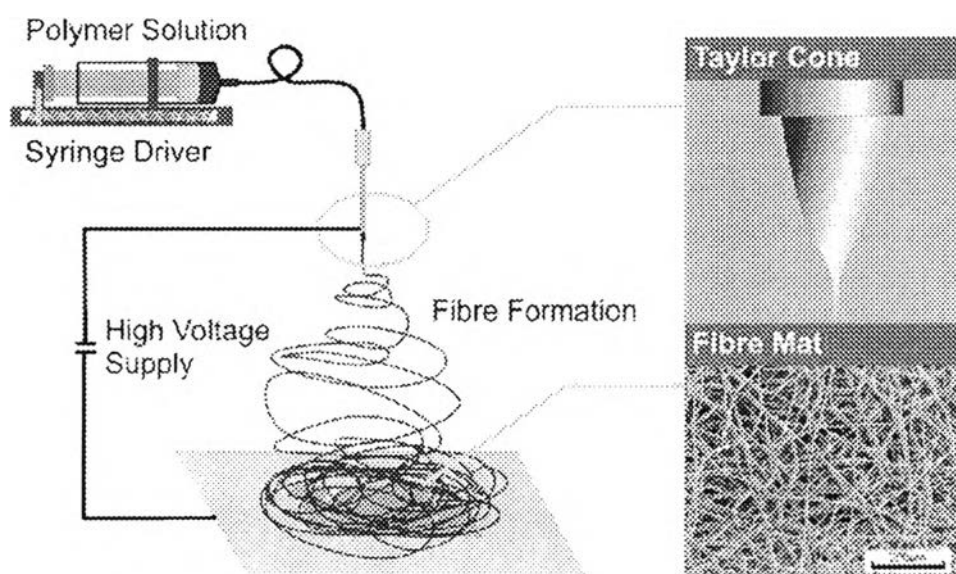


Figure 2.2 Schematic diagram of electrospinning set up.

The random orientation of the electrospun fibers in the typically obtained non-woven webs is acceptable in some applications such as filters, wound dressings and tissue scaffolds. The fiber morphology is controlled by the experimental parameters and is dependent upon solution conductivity, concentration, viscosity, polymer molecular weight, applied voltage, etc. Much work has been done on the effect of parameters on the electrospinning process and morphology of fibers (Gu *et al.*, 2005). During the last 10 years extensive research has been conducted on various aspects of electrospinning. These efforts include spinning in any different polymer and solvent pairs, varying fiber forming conditions, fiber characterization and process modeling. Many improvements of the electrospinning process have been patented or proposed. But almost all of the improvements are involved in either how to spin more fibers during a short time by increasing the number of nozzles or how to collect continuous fibers or yarns through altering collecting set-up or how to change solution properties by simply adding some additives. No literature brings in improvement fixings on changing the electrospinning set-up device which can directly act on any solution prepared for spinning, so that the spinning can become easier and thinner fibers can be produced under the same condition (Wan *et al.*, 2006).

2.3 Platinum Nanoparticles

2.3.1 Preparation of Platinum Nanoparticles

Platinum nanoparticles can be prepared via various methods

2.3.1.1 *Ion Exchange*

Ion exchange is a reversible chemical reaction which an ion from solution is exchanged for a similarly charged ion attached to an immobile solid particle. These solid ion exchange particles are either naturally occurring inorganic zeolites or synthetically produced organic resins. The synthetic organic resins are the predominant type used today because their characteristics can be tailored to specific applications. An organic ion exchange resin is composed of high-molecular-weight polyelectrolytes that can exchange their mobile ions for ions of similar charge from the surrounding medium. Each resin has a distinct number of mobile ion sites that set the maximum quantity of exchanges per unit of resin.

Table 2.1 Selectivity of ion exchange resins in order of decreasing preference.

Strong acid cation exchanger	Strong base anion exchanger
Barium	Iodide
Lead	Nitrate
Calcium	Bisulfite
Nickel	Chloride
Cadmium	Cyanide
Copper	Bicarbonate
Zinc	Hydroxide
Magnesium	Fluoride
Potassium	Sulfate
Ammonia Sodium	
Hydrogen	

2.3.1.2 Incipient Wet Impregnation (IWI)

Impregnation is one of the best known methods of producing catalysts. The principle is to impregnate porous supports with solutions of active components. It is used to produce especially with expensive active component; for instance, noble metals are employed as supported catalysts. Alumina is a widely use support for such technique. After the impregnation, catalyst particles are dried. Also the metal salts added are decomposed to the corresponding oxides by heating. The process is shown as followed:

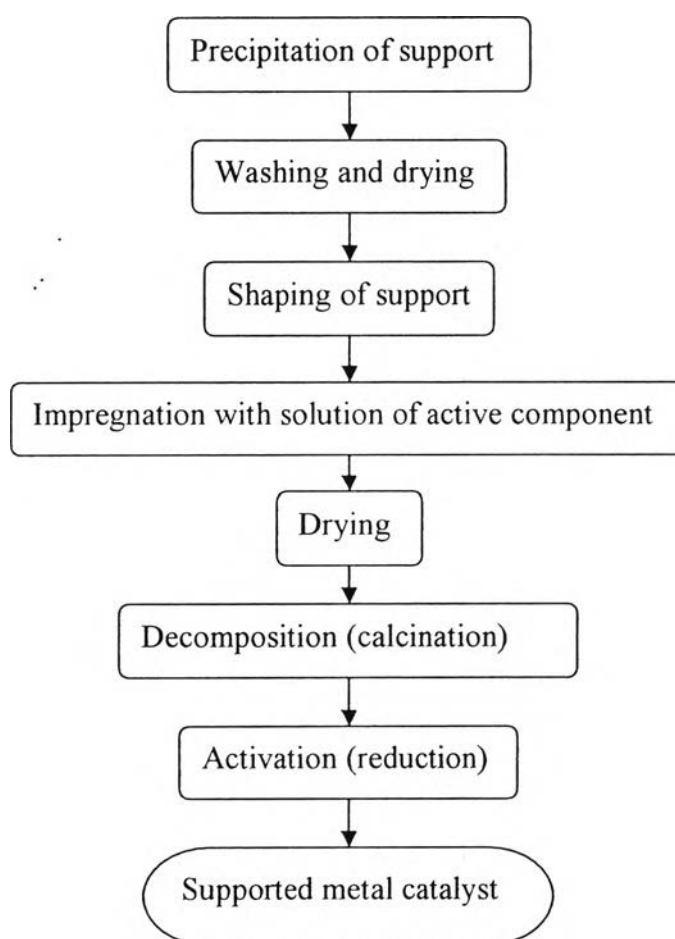


Figure 2.3 Production of supported metal catalysts by impregnation.

During the impregnation process, the active components having unstable anions (e.g. nitrates, acetates, carbonates, and hydroxides) are used. The support is then immersed in a solution of the active component under specific conditions. The selective adsorption of the active component either on the surface or inside of the support depends on the production condition applied. In order to obtain a good impregnation, air in pores of the support needs to be removed by evacuation or treated with carbon dioxide or ammonia gas prior to impregnation. And after the impregnation process, catalyst is dried and calcined.

IWI or incipient wetness impregnation is for large scale manufacture. It is the most advantageous method because the support is brought into contact with a solution, the volume of which corresponds to the total pore volume of the solid and which contains the appropriate amount of precursor. Figure 2.4 demonstrates the principle of the IWI:

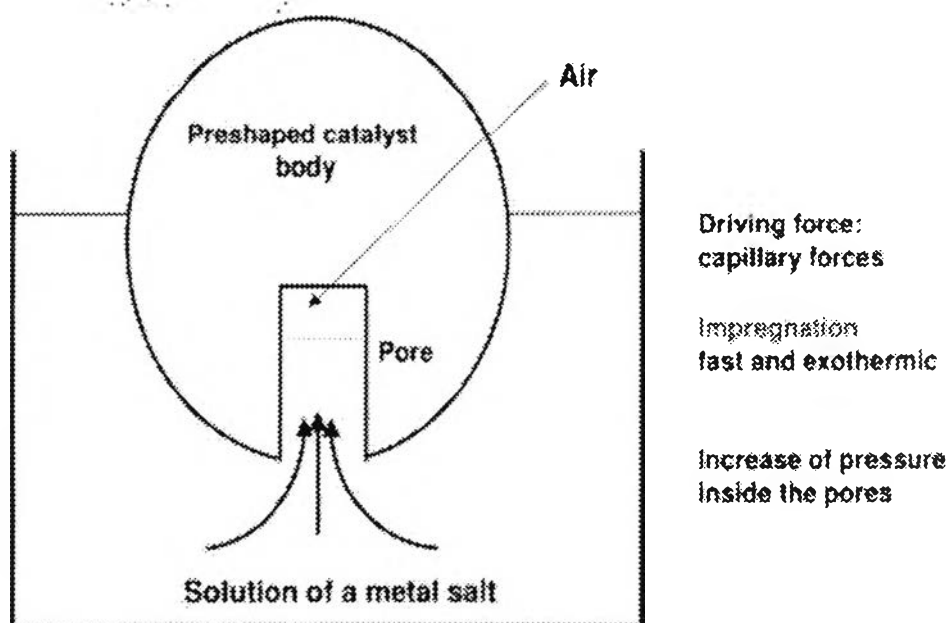


Figure 2.4 Principle of catalyst prepared by incipient wetness impregnation.

2.3.1.4 Chemical Vapor Deposition (CVD)

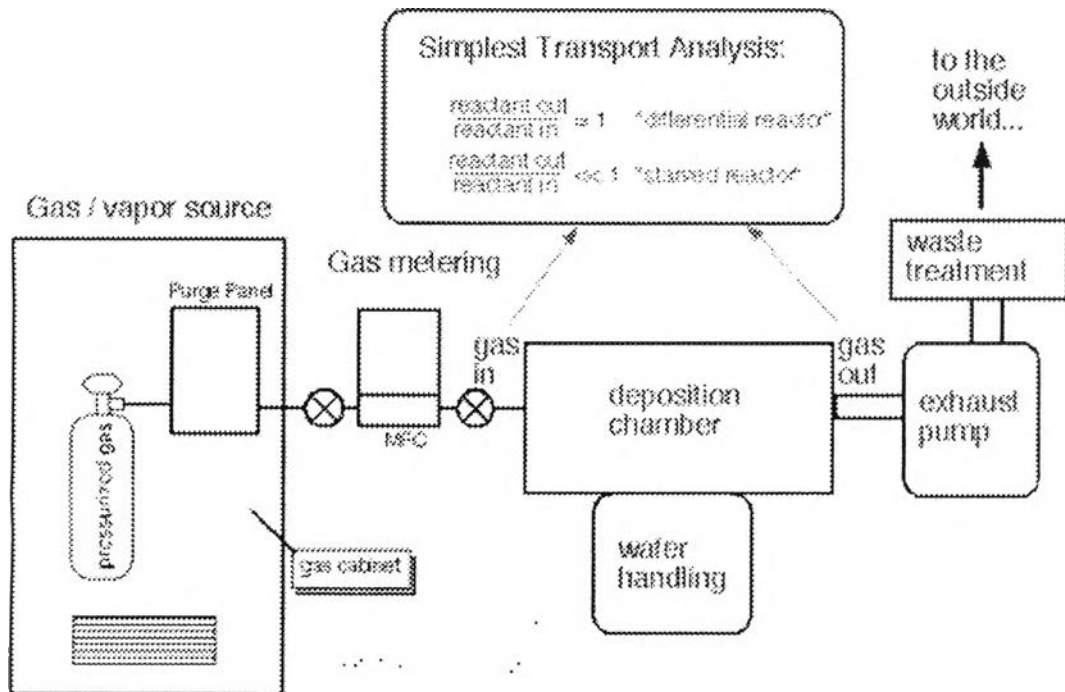


Figure 2.5 General CVD reactor.

Chemical vapor deposition (CVD) is a chemical reaction which transforms gaseous molecules called precursor, into a solid material in the form of thin film or powder, on the surface of a substrate. Typical reactor used for CVD operation is illustrated in figure 2.5. The process is widely used to produce semiconductor devices. A step-by-step fundamental chemical vapor deposition process is shown below:

- Vaporization and transportation of precursor molecules into a reactor
- Diffusion of precursor molecules to surface
- Adsorption of precursor molecules to surface
- Decomposition of precursor molecules on surface and incorporation into solid films
- Recombination of molecular by-products and desorption into gas phase

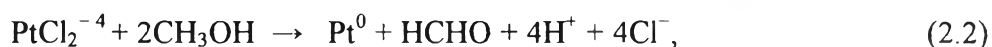
2.3.1.4 Chemical Reduction

Chemical reduction is a simple method of preparing Pt nanoparticles. Chemical reduction process is carried out under high temperature. Conductive heating (reflux and stir) is often used, but microwave dielectric loss heating may be a better synthesis option in view of its energy efficiency, speed, uniformity and simplicity in execution (Chen *et al.*, 2004). In this process, a solution containing the metal precursor salts, reducing agent, and a stabilizer are refluxed at 393–443 K, where the reducing agent decomposes for metal ion reduction.

- Reducing agent

Alcohol

The preparation of Pt nanoparticles by alcohol reduction in the presence of polymer stabilizers is widely practiced. Methanol as the reducing agent has the advantages in generating uniformly distributed nanoparticles. The reaction of H_2PtCl_6 with methanol may take place in two steps:



Lee *et al.* (2006) obtained PtRu(1:1)/C electrocatalysts by polyol method for polymer electrolyte fuel cells. They prepared electrocatalyst using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ as precursors for Pt and Ru, respectively. They applied ethylene glycol as a reducing agent, then stirred and reflux the system at 195°C. Product obtained on carbon substrate was observed to show better distribution of nanoparticles, whereas without carbon as a substrate, nanoparticles seemed to agglomerate.

The synthesis of highly dispersed supported and unsupported PtRu with uniform nanoparticle size remains challenges, especially for unsupported and supported electrocatalysts with high metal loading. Recently, the polyol process is widely used to prepare Pt based supported electrocatalysts. For example, Zhao *et al.* (2006) and Liu *et al.* (2005, 2006) have reported that a microwave radiation is an ef-

ficient method in view of its energy efficiency, speed, uniformity and simplicity in execution to produce Pt/C materials using ethylene glycol as a reducing agent.

Citrate salts

In 2005, Lin *et al.* performed the reduction of hexachloroplatinic acid in solution by citrate. The overall reaction for the reduction of PtCl_2^{-6} by citrate takes place as follows:

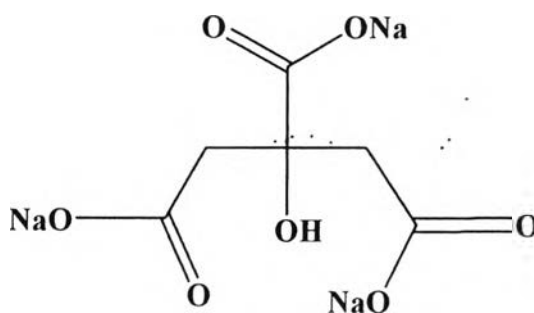
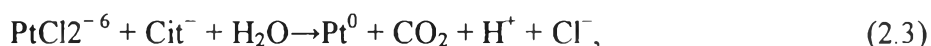


Figure 2.6 The molecular structure of trisodium citrate.

- Stabilizer or Protective Agent

Protective agent is applied to avoid metal particles agglomeration. Good protective agents are removed from the metal nanoparticles easily. There are various chemicals used as protective agents to synthesize Pt nanoparticles reported, polymer (Jiang *et al.*, 2006 and Zuo *et al.*, 1999) and carboxylic anion (Zhao *et al.*, 2006).

Lin *et al.* (2006) showed that the important role of citrate is as a stabilizer. Because of the relatively small size of citrate, it hardly can function as a steric stabilizer like polymers. It is probably stabilizing nanoparticles via electrostatic interaction. When a few drops of sulfuric acid were added to the methanol–citrate sol, immediate precipitation of Pt was observed.

Jiang et al. (2006) has synthesized Pt nanoparticles via polyol process in a presence of polycation, poly (diallyldimethylammonium chloride) (PDDA). The size of Pt nanoparticles colloids was in the range of 2-4 nm which depends on the PDDA to Pt ratio in the solution. This result is useful for direct methanol fuel cells because PDDA-stabilized Pt nanoparticles can block methanol cross over through the Nafion electrolyte membrane and enhance performance of the fuel cells.

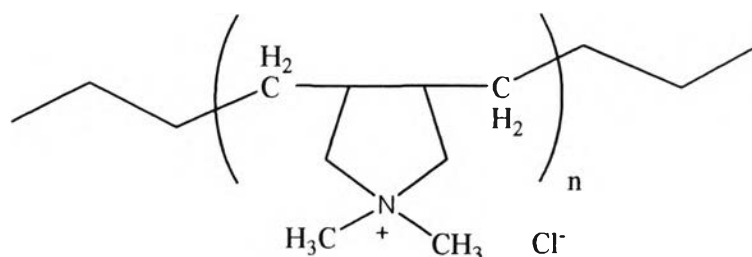


Figure 2.7 Molecular structure of PDDA

Lou (2007) has shown that 3-thiophenemalonic acid can reduce platinum precursor and stabilize Pt nanoparticled obtained simultaneously during microwave radiation. The particle size was between 1-5 nm depends on molar ratio between 3-thiophenemalonic acid and H_2PtCl_6 .

2.3.2 Optical Properties of Platinum Nanoparticle

Conduction electrons and ionic cores in metal form a plasma state. When external electric fields (electro-magnetic waves, electron beams etc.) are applied to a metal, electrons move so as to screen perturbed charge distribution, further move beyond the neutral states, and again return to the neutral states and so on. This collective motion of electrons is called a “Plasma Oscillation” as shown in Figure 2.7. The surface plasmon resonance is a collective excitation mode of the plasma localized near the surface. Electrons confined in a nanoparticle conform the surface plasmon mode. The resonance frequency of the surface plasmon is different from an ordinary plasma frequency. The surface plasmon mode arises from the electron confinement in the nanoparticle. Since the dielectric function tends to become continuous at the interface (surface), the oscillation mode shifts from the ordinary plasma resonance and exponentially decays along the depth from the surface.

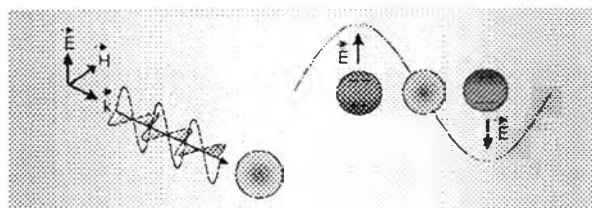


Figure 2.8 Plasmon oscillation of the free electron on the surface of metal nanoparticle.

2.3.3 Catalytic Activity of Pt Nanoparticles

It is well known that the catalytic activity of the metal is strongly dependent on the particle shape, size and size distribution. There are many important reactions catalyzed by platinum; for instance, oxidation of carbon monoxide at low temperature (Tang *et al.*, 2005), hydrogenation reactions (Toebe *et al.*, 2004), methanol oxidation (Zhao *et al.*, 2006), oxygen reduction (Wei *et al.*, 2005) and hydrogen electro-oxidation (Zhou *et al.*, 2007).

Hydrogenation of cinnamaldehyde is one among those hydrogenation reactions catalyzed by Pt particles which gives various products, hydrocinnamaldehyde, cinnamyl alcohol, and phenyl propanol which are typically used in perfumery and pharmaceuticals (Hongxia Ma *et al.*, 2007). These products can be obtained through the selective hydrogenation of conjugated C=C or C=O. The study showed that two kinds of carbon nanotubes (CNTs) with different inner diameter (less than 10 nm: CNTs-1 and between 60 and 100 nm: CNTs-2) were used as catalyst supports. The platinum particles were simply deposited on the outside surface (CNTs-1) and inside (CNTs-2) and were easily reduced to Pt⁰ by refluxing. The catalysts exhibit high activities in the selective hydrogenation of cinnamaldehyde. But the selectivity of these two catalysts was quite different under same reaction conditions. The high selective hydrogenation of C=O bond was observed over catalyst 3%Pt/CNTs-2, while the completely hydrogenation of both C=C and C=O bonds was found over catalyst 3%Pt/CNTs-1.

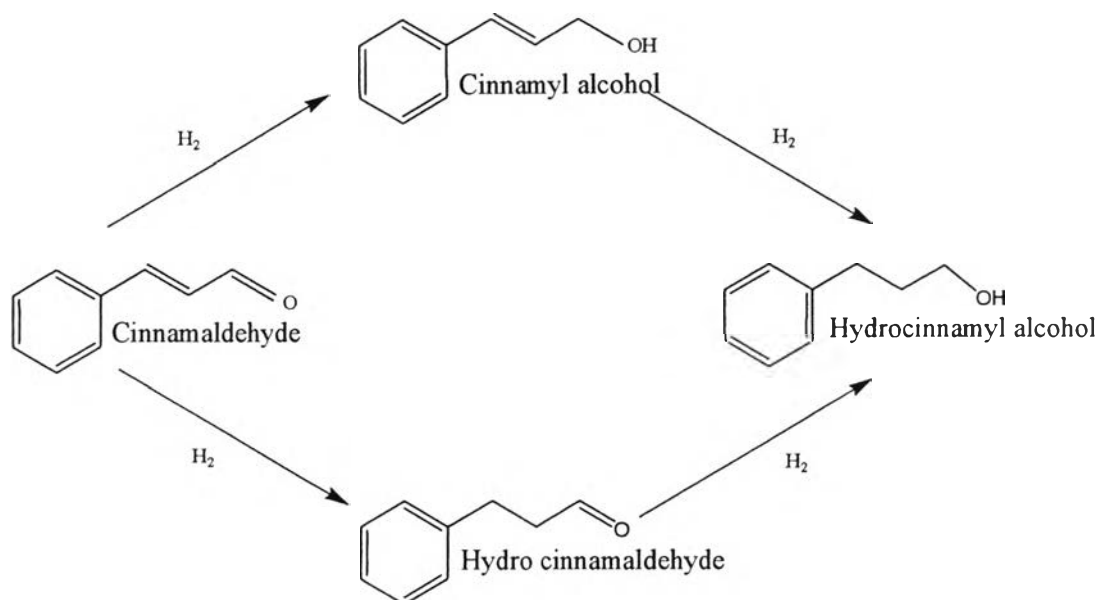


Figure 2.9 The hydrogenation of cinnamaldehyde (CAL) produces a mixture of cinnamyl alcohol (COL), hydrocinnamaldehyde (HCAL) and hydrocinnamyl alcohol (HCOL) depending on reaction conditions used.

Jinghong Ma *et al.* (2005) prepared PVP-Pt nanoclusters supported zeolite catalysts by IWI method for converting methane to higher hydrocarbon at low temperature. The result indicated that the activity of catalysts increases for methane conversion with decrease of particle size, and the distributions of C₂⁺ products vary in favour of the heavier hydrocarbons as the particle size increase.

Jie Zhao *et al.* (2006) studied the methanol electro-oxidation catalyzed by Pt particles produced via chemical reduction process with acetate and without acetate ions as a stabilizer. A better electrocatalytic performance for methanol oxidation by the Pt/C catalyst prepared by adding proper acetate to the polyol solution was demonstrated by cyclic voltammetry and chronoamperometry. The improvement in electrocatalytic performance was because the Pt/C catalyst prepared by the microwave polyol process had small, uniform and highly dispersed Pt nanoparticles when the proper amount of acetate solution was added to the synthesis solution.