#### THE PREPARATION AND ANALYSIS OF NEW CARBON SUPPORTED Pt AND Pt+SECOND METAL NANOPARTICLES CATALYSTS FOR DIRECT METHANOL FUEL CELLS

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FATİH ŞEN

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# THE PREPARATION AND ANALYSIS OF NEW CARBON SUPPORTED Pt AND Pt+SECOND METAL NANOPARTICLES CATALYSTS FOR DIRECT METHANOL FUEL CELLS

submitted by FATIH ŞEN in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry Department, Middle East Technical University by,

Prof. Dr. Canan Özgen Dean, Graduate School of <b>Natural and Applied Sciences</b>		
Prof. Dr. İlker Özkan Head of Department, <b>Chemistry</b>		
Prof. Dr. Gülsün Gökağaç Arslan Supervisor, <b>Chemistry Department</b> , <b>METU</b>		
Examining Committee Members:		
Prof. Dr. İnci Eroğlu Chemical Engineering Dept., METU		
Prof. Dr. Gülsün Gökağaç Chemistry Dept., METU		
Prof. Dr. Ceyhan Kayran Chemistry Dept., METU		
Assoc. Prof. Dr. Ayşen Yılmaz Chemistry Dept., METU		
Assoc. Prof. Dr. Metin Aydin Chemistry Dept., 19 Mayis University		
	Date:	25/09/2012

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all materials and results that are not original to this work.

Name, Last name: Fatih ŞEN

Signature:

#### ABSTRACT

# THE PREPARATION AND ANALYSIS OF NEW CARBON SUPPORTED Pt AND Pt+SECOND METAL NANOPARTICLES CATALYSTS FOR DIRECT METHANOL FUEL CELLS

Şen, Fatih PhD., Department of Chemistry Supervisor: Prof. Dr. Gülsün Gökağaç Arslan

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In this thesis, firstly, carbon-supported platinum nanoparticle catalysts have been prepared by using PtCl<sub>4</sub> and H<sub>2</sub>PtCl<sub>6</sub> as starting materials and 1-hexanethiol, and tertoctanethiol, as surfactants for the first time. Secondly, these prepared catalysts were heated to 200 °C, 300 °C, and 400 °C for 4 h under argon gas. Lastly, PtRu/C catalysts, which have different atomic percent ratios of Pt and Ru (Pt/Ru: 0.8, 2.1 and 3.5), were prepared using  $PtCl_4$  and  $RuCl_3$  as starting materials and tertoctanethiol as a surfactant. Each was characterized by X-ray diffraction, transmission electron microscopy, energy dispersive analysis, X-ray photoelectron spectroscopy, cyclic voltammetry, and elemental analysis, and their activities were determined toward the methanol oxidation reaction. It has been found that all prepared catalysts are more active toward methanol oxidation reaction compared to the commercial catalysts. It was also found that increasing the temperature during the heat treatment process results in an enlargement of platinum particle size and a decrease in catalytic activity in the methanol oxidation reaction. Transmission electron microscopy shows that platinum nanoparticles are homogeneously dispersed on the carbon support and exhibited a narrow size distribution with an average particle size of about 2-3 nm in diameter. X-ray photoelectron spectra of all catalysts indicated that most of the platinum nanoparticles (> 70 %) have an oxidation state of zero and rest (< 30 %) have a +4 oxidation state with (Pt  $4f_{7/2}$ ) binding energies of 71.2-72.2 and 74.3-75.5 eV, respectively.

**Keywords:** Direct Methanol Fuel Cells, Platinum Nanoparticles, Platinum-Ruthenium Catalysts, Cyclic Voltammetry, Transmission Electron Microscopy, Xray Photoelectron Spectroscopy.

# DOĞRUDAN METANOL YAKIT PİLLERİ İÇİN YENİ KARBON DESTEKLİ Pt ve Pt+İKİNCİ METAL NANOPARÇACIKLI KATALİZÖRLERİN HAZIRLANMASI VE ANALİZLERİ

Şen, Fatih Doktora, Kimya Bölümü Tez Yöneticisi: Prof. Dr. Gülsün Gökağaç

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Bu tezde, ilk olarak karbon destekli platin nanoparçacıklı katalizörler PtCl<sub>4</sub> ve H<sub>2</sub>PtCl<sub>6</sub> başlangıç maddeleri ile, 1-hekzantiol ve tert-oktantiol (ilk kez) gibi sürfaktanlar kullanılarak hazırlandı. Daha sonra hazırlanan bu katalizörler parçaçık boyutlarını değiştirebilmek amacıyla 4 saat boyunca 200, 300 ve 400 °C ` de ısıl isleme tabii tutuldu. Son olarak, tert-oktantiol sürfaktanın yardımıyla. Pt ve Ru elementlerinin yüzde oranları 0.8, 2.1 ve 3.5 olacak şekilde üç katalizör daha hazırlandı ve hazırlanan tüm katalizörler X-ışını kırınımı, geçirmeli elektron mikroskobu, X-ışınları mikroskobu, dönüşümlü voltametri vb yardımıyla karakterize edildi. Hazırlanan tüm katalizörlerin methanol yükseltgenme reaksiyonu için ticari katalizörlere göre çok daha aktif olduğu görüldü. Ayrıca ısıl işlem sırasında, daha yüksek sıcaklığa kadar ısıtılan katalizörlerde parçaçık boyutunun arttığı ve methanol yükseltgenme reaksiyonuna karşı daha düşük aktivite elde edildiği tespit edildi. Geçirmeli elektron mikroskobu, hazırlanan tüm katalizörlerin karbon destek üzerinde homojen olarak dağıldığını ve ortalama parçaçık boyutlarının yaklaşık 2-3 nm olduğunu gösterdi. Ayrıca, x-ışını fotoelektron spektroskopisi ile Pt 4f bölgesi incelendiğinde, hazırlanan katalizörlerde platinlerin % 70 den fazlası sıfır değerlikli (71.2 ile 72.2 eV arasında) geri kalan kısmının ise +4 değerlikli (74.3 ile 75.5 eV arasında) olduğu gözlendi.

Anahtar Kelimeler: Doğrudan Metanol Yakıt Pilleri, Platin Nanoparçacıkları, Karbon Destekli ve Tiol ile Stabilize Edilmiş Katalizörler, Dönüşümlü Voltametre, Transmisyon (Geçirmeli) Elektron Mikroskopisi.

To My Family

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#### **CHAPTER 1**

#### INTRODUCTION

#### **1.1. ENERGY and FUEL CELLS**

One of the basic requirements of our life is the energy and it is not possible to survive our life without it. Generally, energy is the ability to do work or transfer heat and it can be in different forms (Kutz, 2007):

- Heat (thermal)
- Light (radiant)
- Motion (kinetic)
- Electrical
- Chemical
- Nuclear energy
- Gravitational

Energy sources can be divided into two groups, such as renewable and nonrenewable. Those energy sources generally produce some secondary energy sources. For instance, nonrenewable energy sources include the fossil fuels such as oil, natural gas, and coal. Those type of conventional energy sources will run out in the near future, for example the investigations show that petroleum and coal will be finished in 50-70 years. Therefore, scientists have been working on the alternative energy sources which will not run out and will be produced cheaply and environment friendly. These are solar, wind, hydropower, biomass, geothermal energy sources and fuel cells. It is also well known that fuel cells are one of the most important alternative energy for as long as fuel and oxidant are supplied. Fuel cells consist of an anode (negative side), a cathode (positive side) and an electrolyte that allows charges to move between the two sides of the fuel cell. Generally, fuel cells have lots of advantages compared to other types of conventional power sources (Bagotsky, 1967, 1977 and 2009);

## (i) Efficiency

In conventional energy sources, there are three steps for the conversion of the chemical energy of a fuel into the electrical energy as shown in Figure 1.1. In the first step, fuels are burnt to produce heat, then thermal energy is used to convert water to stream which is used to produce mechanical energy in steam turbines and lastly, this mechanical energy is converted to the electrical energy by an alternator. However, in fuel cells chemical energy is converted directly into electricity without a preliminary conversion into heat and no mechanical conversion is required such as boiler-to-turbine and turbine-to-generator systems. Although 100% efficiency is possible from fuel cells, in practice, 50% or greater efficiency is observed with current technology (Gokagac, 1994).



**Figure 1. 1**. The principle of fuel cell technology compared to conventional energy production

#### (ii) Maintenance and Manufacturing

Most fuel cells show little or no maintanance problems since there are few or no moving parts in the system. Sealing problems are minimum and the manifacturing cost of fuel cells are very low compared to the classical engines (Zhao, 2007).

#### (iii) Cleanliness

The combustion of fossil fuels results in the production of large amount of sulfurdioxide, nitrogen oxides and carbon dioxide. If combustion is not complete, it yields carbon monoxide, a variety of hydrocarbons and soot (carbon particles). Those pollutants give rise to some environmental effects such as acid rain and greenhouse effect. However, in most fuel cells under consideration today for practical application there are no noxious fumes or other objectionable combustion products. End products are usually water, carbon dioxide. Unspent fuels and oxidants can be recirculated and electrolytes are totally enclosed or isolated from exhaust systems. (Gokagac, 1994).

#### (iv) Weight, Volume and Capacity

The performance of the power systems is often defined by power-per-unit-volume and power-per-unit-weight. Fuel cells have higher performance and overload capacity compared to batteries (Davytyan, 1947).

#### (v) Noise and Heat

Fuel cells provide silent electrical power generator compared to internal combustion engines because of no or few moving parts in those cells. Moreover, fuel cells also have the minimized detectable heat loss. Those properties are big advantages in military and communication applications (Hoogers, 2003).

#### **1. 2. THE HISTORY OF FUEL CELLS**

British scientists Sir Anthony Carlisle and William Nicholson discovered the decomposition of water into hydrogen and oxygen using electricity (water electrolysis) before the fuel cell. Both scientists connected one end of a pair of conducting wires to the electrodes of the battery, while the other end was arranged in a saline solution in order to accumulate hydrogen and oxygen gas (from water) at the ends of the electrodes (Srinavasan, 2006).

#### **1.2. 1. THE "GASEOUS VOLTAIC BATTERY"**

The concept of hydrogen fuel cell which was introduced by Sir William Robert Grove in 1838 is the reverse of electrolysis as shown in Figure 1. 2.. Grove discovered a " gaseous voltaic battery "- which is the first fuel cell (Grove, 1839). This fuel cell was arranged by two platinum electrodes with one end of each immersed in a container of sulfuric acid and the other ends separately sealed in containers of oxygen and hydrogen, a constant current would flow between the electrodes. The sealed containers held water as well as the gases, and he noted that the water level rose in both tubes as the current flowed. He combined the several sets of these electrodes (50 monocells with two-dimensional platinum electrodes 31.75 mm wide) in a series circuit for the formation of the fuel cell, Figure 1. 3. (Davytyan, 1947). In 1889, Ludwig Mond and Car Langer described the process with a hydrogen-oxygen fuel cell that attained 6.5 mA/cm<sup>2</sup> (electrode area) to 0.73 V, with perforated platinum electrodes (Mond and Langer, 1899). After the demonstration by Mond and Langer of their gas battery, Alder Wright and Thompson brought attention to their "aeration plate" electrodes that also acted as a matrix to

contain the electrolyte. In the same year, Lord Rayleigh reported the use of platinum gauze as an electrode with higher surface area. Also Rayleigh, and later Mond and Langer used a "direct coal" fuel cell derived from coal (Hoogers, 2003).



**Figure 1. 2.** The principle of an electrolyzer, shown left; of a fuel cell, shown right (Hayre, 2009).



**Figure 1. 3.** Grove's 'gas battery' (1839) produced a voltage of about 1 volt, shown left. Grove's 'gas chain' powering an electrolyzer (1842), shown right (Hayre, 2009).

# 1.2. 2. " ELECTRICITY FROM DIRECT COAL"

In 1894, Friedrich Wilhelm Ostwald, which is considered the founder of the chemistry–physics, in 1893, proposed to produce electricity from coal by electrochemical process as the solution to the inefficient energy conversion (from chemical energy in coal to mechanical energy in a steam engine) process but it was uncertain how the galvanic item would be created. The interconnection of various components of a fuel cell such as electrodes, electrolyte, oxidizing and reducing agents, anions and cations was experimentally determined by Ostwald. Ostwald, drawing on their pioneering work related to the physical properties and chemical reactions in fuel cells, solved the puzzle of Grove's gas battery. Ostwald`s research was the basis for further research in the chemistry of fuel cells (Ostwald, 1894).

In 1896, Jacques built fuel cells (Jacques, 1897) to produce electricity from coal and then Haber and Bruner (1904) (Haber and Bruner, 1904 and 1906) determined the electrochemical reaction between the coal and the electrolyte, and then with the electrode; therefore, they concluded that the Jacques cell was "indirect" instead of the direct oxidation of coal.

In 1935, Baur and Ehrenberg, who found that  $CO_2$  supplied to the cathode improved the performance of the fuel cell, used a mixture of alkali metal carbonates after they tested several types of electrodes, including hydroxide, carbonate, silicate, and borate. Baur and Brunner (1937) concluded that a solid electrolyte was more suitable and they began investigating ceramic materials since the molten electrolyte flooded the electrodes (Bagotsky, 2009).

#### **1.2. 3. THE SOLID OXIDE FUEL CELL (SOFC)**

In 1900, William Nernst (Nernst, 1912) prepared electrical lamps including the oxides of zirconium, thorium, yttrium, and the rare earth elements, which emitted nearly pure white light compared to the "strongly reddish light of the normal lamps". He found that the pins began emitting light between 500 and 700 °C depending on their composition. In 1937, Baur and Preis (Baur and Preis, 1937) developed the solid oxide fuel cell (Figure 1. 4) using these solid oxide lamps that had been developed by Nerst. Generally, a solid oxide single fuel cell consist of four layers (three of them are ceramics) stacked together is typically only a few millimeters thick. When hundreds of these cells are connected in series then they form an "SOFC stack". These type of fuel cell needs very high temperature ranging from 500 to 1000 °C to activate the ceramics used in SOFCs electrically and ionically. Figure 1. 4 summarizes the electrochemical reactions occurring within the SOFC (Basu, 2007);

At the cathode:

 $\frac{1}{2}$  O<sub>2</sub> + 2e<sup>-</sup>  $\rightarrow$  O<sup>2-</sup>

At the anode:

 $H_2 + \frac{1}{2} O^{2-} \rightarrow H_2O + 2e^-$ 

The overall cell reaction:

 $1/2 O_2 + H_2 \rightarrow H_2O$ 



**Figure 1. 4.** Scheme of a solid-oxide fuel cell (http://www1.eere.energy.gov/hydrogenandfuelcells/fuelcells/fc\_types.html)

#### 1.2. 4. THE MOLTEN CARBONATE FUEL CELL (MCFC)

Alkali metal carbonates were used for the development of the "direct coal" fuel cell, but they emerged from the other salts because of their compatibility with the products of the oxidized fuel. Similar to the SOFC, the Molten Carbonate Fuel Cells (MCFC) (Figure 1. 5) operate at temperature of 1100 to 1300 °F or 600 to 700 °C in order to keep the alkali carbonates in a highly conductive molten salt form, the carbonate ions providing ionic conduction. The electrolyte typically consists of a combination of alkali (Na and K) carbonates retained in a ceramic matrix of LiAlO<sub>2</sub>. The anode is made from Ni while the cathode is made from nickel oxide.

The electrochemical reactions occurring in the cell are:

At the anode:

 $H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^{-}$ 

At the cathode:

 $1/2 O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$ 

The overall cell reaction:  $H_2 + 1/2O_2 + CO_2$  (cathode) =  $H_2O + CO_2$  (anode)



**Figure 1. 5.** Scheme of a molten carbonate fuel cell (http://www1.eere.energy.gov/hydrogenandfuelcells/fuelcells/fc\_types.html)

The primary disadvantage of current MCFC technology is durability. The high temperatures at which these cells operate and the corrosive electrolyte used accelerate component breakdown and corrosion, decreasing cell life. Scientists are currently exploring corrosion-resistant materials for components as well as fuel cell designs that increase cell life without decreasing performance (Davytan, 1946).

#### **1.2. 5. THE ALKALINE FUEL CELL (AFC)**

The alkaline fuel cell (Figure 1. 6), also known as the Bacon fuel cell after its British inventor, is one of the most developed fuel cell technologies (Bacon, 1960). These

fuel cells use a solution of potassium hydroxide in water as the electrolyte and can use a variety of non-precious metals as a catalyst at the anode and cathode. Briefly, the electrochemical reactions inside an AFC are:

Anode reaction;  $2 H_2 + 4 OH^- \rightarrow 4 H_2O + 4 e^-$ Cathode reaction;  $O_2 + 4 e^- + 2 H_2O \rightarrow 4 OH^-$ Overall reaction;  $2H_2 + O_2 \rightarrow 2H_2O$ 

High-temperature AFCs operate at temperatures between  $100^{\circ}$ C and  $250^{\circ}$ C. However, newer AFC designs operate at lower temperatures of roughly  $23^{\circ}$ C to  $70^{\circ}$ C. The disadvantage of this fuel cell type is that it is easily poisoned by carbon dioxide (CO<sub>2</sub>). In fact, even the small amount of CO<sub>2</sub> in the air can affect this cell's operation, making it necessary to purify both the hydrogen and oxygen used in the cell. This purification process is costly. Susceptibility to poisoning also affects the cell's lifetime (the amount of time before it must be replaced), further adding to cost (Sammes, 2006).



**Figure 1. 6.** Diagram of an Alkaline Fuel Cell. (http://www1.eere.energy.gov/hydrogenandfuelcells/fuelcells/fc\_types.html)

#### **1.2. 6. THE PHOSPHORIC ACID FUEL CELL (PAFC)**

PAFCs (Figure 1. 7), that was invented in the mid-1960s, are another type of fuel cell that uses liquid phosphoric acid as an electrolyte. In 1975, the phosphoric acid fuel cell was developed during the TARGET program, which met its goal of demonstrating the technology as electrical power systems for houses supplied with natural gas. The fuel cell systems produced 12.5 kW of electricity, and after this program fuel cell power plants of megawatt (MW) size were tested. They were the first fuel cells to be commercialized due to high stability, performance and low cost.

This type of fuel cells use highly concentrated phosphoric acid  $(H_3PO_4)$  solution that is saturated in a silicon carbide matrix (SiC) as an electrolyte and carbon paper coated with Pt catalyst as an electrode. Generally, operating range is between 150 and 210  $^{\circ}$ C.

Briefly, the electrochemical reactions inside an PAFC are:

Anode:  $H_2 \rightarrow 2H^+ + 2e^-$ Cathode:  $1/2 O_2 + 2H^+ + 2e^- \rightarrow H_2O$ Overall:  $H_2 + 1/2 O_2 \rightarrow H_2O$ 

At the anode, hydrogen is split into two hydrogen ions  $(H^+)$ , which pass through the electrolyte to the cathode, and two electrons which pass through the external circuit (electric load) to the cathode. At the cathode, the hydrogen, electrons and oxygen combine to form water.



**Figure 1. 7.** Diagram of an phosphoric acid fuel cell (http://www1.eere.energy.gov/hydrogenandfuelcells/fuelcells/fc\_types.html)

### **1.2. 7. THE SOLID POLYMER FUEL CELL**

In 1960, Grubb and Niedrach developed the solid polymer fuel cell at General Electric. In this type of fuel cell, the solid polymer was an acidic polymer, which would allow to use with CO<sub>2</sub> without reacting with the gas. After Grot and Raistick improved a new polymer formulation and electrode fabrication for the performance and durability of the electrolyte and the fuel cell was seen more practical for road vehicles. In the early 1970s, this type of fuel cell was called a "solid polymer electrolyte fuel cell" (SPEFC) but after the proton exchange mechanism (PEM) was well-understood, this was called 'Proton Exchange Membrane Fuel Cells (PEMFC)' as shown in Figure 1. 8. PEM fuel cells use a permeable solid polymer membrane (a

thin plastic film) as the electrolyte. This membrane does not conduct electrons. First used in the 1960s for the NASA Gemini program, PEMFCs are currently being developed and demonstrated for systems ranging from 1 W to 2 kW.

Hydrogen and hydrogen ion  $(H^+)$  can be used as fuel and charge carrier in the PEMFC. At the anode, the hydrogen molecule is split into hydrogen ions (protons) and electrons. The hydrogen ions permeate across the electrolyte to the cathode while the electrons flow through an external circuit and produce electric power. At the cathode oxygen, usually in the form of air, reacts with the electrons and the hydrogen ions to produce two moles of water. The reactions at the electrodes are as follows:

At the anode:  $2H_2 \rightarrow 4H^+ + 4e^-$ At the cathode:  $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ Overall :  $2H_2 + O_2 \rightarrow 2H_2O$ 

Compared to other types of fuel cells, PEMFCs generate more power in lower operating temperature (less than 100°C) for a given volume or weight of fuel cell. This high-power density characteristic makes them compact, lightweight and the top candidate for automotive power applications (Broers, 1960).

Other advantages of PEMFC related to the electrolyte being a solid material, compared to a liquid. The solid electrolyte is also less expensive to manufacture, more immune to difficulties with orientation and has less problems with corrosion, compared to many of the other electrolytes, thus leading to a longer cell and stack life.

The biggest problem in these type of fuel cells is the hydrogen storage. Generally, hydrogen can be stored in a number of ways, including compressed gas, chemical compounds, liquid hydrogen or metallic hydrogen but those methods are costly for the commercialization of these fuel cells.



**Figure 1. 8.** Diagram of an PEMFC. (http://www1.eere.energy.gov/hydrogenandfuelcells/fuelcells/fc\_types.html)

## **1.2. 8. THE DIRECT METHANOL FUEL CELL (DMFC)**

The methanol electro-oxidation process was explored for the first time by E. Muller in 1922 (Apanel, 2004). In 1951, Kordesch and Marko constructed the first fuel cell based on this concept (Kordesch, 1996). Industrial DMFC development started about a decade later with the development of a 100W unit for military applications by Ciprois et al. (Ciprois, 1967). The specific development of methanol electrooxidation catalysts was driven by the work done in industrial laboratories during 1960s and 1970s, namely, at Shell (Williams, 1968) and at General Electric. During the early 1960s, after General Electric produced the fuel-cell-based electrical power system for NASA's Gemini and Apollo space capsules, Dr. Lawrence H. DuBois of (U.S. Department of Defense and the Defense Advanced Research Projects Agency (DARPA)) decided the development of a liquid hydrocarbon fuel cell that will use methanol, etcas fuel. Dr. Dubois called on Dr. Surya Prakash and Nobel laureate Dr. George A. Olah, (both of them were from the University of Southern California's (USC) Loker Hydrocarbon Institute) in order to invent such a fuel cell. USC, Jet Propulsion Laboratory (JPL) from California Institute of Technology (Caltech) collaborated to invent Direct Methanol Fuel Cell (DMFC), Technology. Department of Trade and Industry (DTI) company acquired the exclusive worldwide license for Direct Oxidation of Liquid Hydrocarbons, DMFC Technology. DTI's President and CEO, Todd Marsh, saw the future impact that a clean alternative to fossil fuels was being born and offered to steward this technology.

DMFCs are a subcategory of proton-exchange fuel cells in which methanol is used as the fuel. In the last forty years, direct methanol fuel cells (DMFCs) are widely investigated and considered as attractive power sources compared to other types of fuel cells since DMFC has lots of spesific advantageous including

(a) Methanol is readily available from coal, natural gas, and cheap in comparison to other hydrocarbons.

(b) Although methanol has a lower electro-activity in acid solutions than formaldehyde or formic acid (Schlatter, 1963; Vielstich, 1970), it is a better fuel because of its potentially higher energy content per unit mass (Liebhavskky and Cairns, 1968; Cathro and Weeks, 1971).

(c) High efficiencies of fuel cells compared to internal combustion engines result in a more environmentally acceptible power source. Also the lack of sulfur and nitrogen additives in the fuel means there is no  $SO_2$  or  $NO_x$  production. This makes methanol an environmentally better fuel than any petroleum product, natural or synthetic.

(d) Methanol is a liquid fuel, therefore it is easier to store and transport than gaseous fuels and is soluble in aqueous media, which allows a wide range of solvents to be used.

(e) Methanol is oxidized at room temperatures, which would make it suitable for use in cars and other vehicles (Mcnicol, 1977, 1978 and 1981).

(f) The DMFC is relatively low weight compared to the internal combustion engine or conventional storage batteries. It is small enough to serve as an automobile engine (Mcnicol, 1977, 1978 and 1981).

(g) There are few moving parts in a DMFC, thus decreasing the chance of mechanical failure, leading to reduced maintenance and simplicity of working.

(h) If a cheap electro-oxidative catalyst can be found for methanol then it will be more reactive under acidic conditions than many other fuels (Gokagac, 1994). The DMFC relies upon the oxidation of methanol on a catalyst layer to form carbon dioxide. Water is consumed at the anode and is produced at the cathode. Protons ( $H^+$ ) are transported across the proton exchange membrane - often made from Nafion - to the cathode where they react with oxygen to produce water. Electrons are transported through an external circuit from anode to cathode, providing power to connected devices (Figure 1.9)

The half-reactions are:

Anode reaction:

 $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ 

Cathode reaction:

$$3/2 \text{ O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3 \text{ H}_2\text{O}$$

Overall reaction:



**Figure 1. 9.** Schematic of a DMFC employing an acidic solid polymer electrolyte membrane.

#### **1.3. THE NEED FOR A CATALYST**

Although methanol has a lot of advantages to use in direct methanol fuel cells, it has poor electrochemical reactivity in acid solutions, which limits its use for practical purposes. Consequently, a catalyst is neeeded to activate the methanol. The active electrocatalysts in acid medium are platinum-group metals, in particular Pt itself (Bockris and Srinivasan, 1969; Mcnicol, 1977, 1978 and 1981; Bockris et al., 1981). The high cost and rapid poisoning of platinum metal has motivated researchers to find an alternative affordable catalyst. In order to solve this problem, the mechanism of the electrooxidation of methanol in aqueous solution has been extensively studied over the last four decades (Williams, 1966; Bockris and Srinivasan, 1969).

# 1. 4. THE MECHANISM OF METHANOL ELECTROOXIDATION ON PLATINUM IN ACID SOLUTIONS

To understand the mechanism of oxidation reaction on methanol at Pt-related electrodes is very important for the development of DMFCs, (Parsons, 1988; Iwasita 1990) Therefore, it is possible to find extensive studies on this subject. (Wasmus, 1995; Li, 1997; Watanabe, 1973; Mottoo, 1976). For instance, Iwasita et al used alkaline electrolytes for methanol fuel cells and examined nickel or platinum for the methanol oxidation reaction (MOR) as an anode catalyst and silver for the oxygen reduction process as a cathode catalyst (Iwasita, 1990). Parallel investigations of the MOR were also examined for acidic electrolytes like sulfuric acid and it was found that the kinetics of MOR was slower in an acidic electrolyte compared to the alkaline ones. The main problem of a liquid alkaline electrolyte (KOH) is that this electrolyte react with carbon dioxide that is the reaction product of methanol oxidation, to give rise to the formation of carbonate. Hence, the major studies have been conducted in the acid electrolyte conditions. Generally, the anodic oxidation of methanol on Pt in acidic electrolyte is a process of six-electron transfer per methanol molecule, where the thermodynamic potential is 0.04 V vs reversible hydrogen electrode, very close to the hydrogen electrode potential (Xia, 1996). However, it is believed that the
adsorbed intermediates in the reaction are difficult to oxidize, causing an overpotential of several hundred millivolts until reasonable reaction rates can be observed (Parsons, 1988). The main obstacle to an efficient DMFC is the rapid decrease in the activity of Pt (the most effective electrocatalyst as a single metal) for methanol electro-oxidation; this is generally associated with the buildup of "strongly adsorbed" methanol fragments on the Pt surface (McNicol, 1981), which act as poison. These are linear or bridge  $CO_{ads}$  and other intermediates that is thermodynamically possible such as  $(CH_xOH)_{ad}$ ,  $(-COH)_{ad}$ , formyl  $(-HCO)_{ad}$ , carboxy (-COOH)<sub>ad</sub>, or a dimer of formic acid  $(HCOOH)_{2ad}$  (Parsons et al, 1988; Ivasita et al, 2002; Beden et al, 1987).

Many spectrometry techniques such as in situ IR spectroscopy, differential electrochemical mass spectrometry (DEMS), electrochemically modulated infrared reflection spectroscopy (EMIRS) etc have been used to identify the adsorbed species formed during the electro-oxidation of methanol, (Juanto, 1987; Kunimatsu, 1987). EMIRS has also been used to identify the linear bonded CO (CO<sub>L</sub>) and bridged CO (CO<sub>B</sub>) (Beden, 1982). Linear potential sweep infrared reflection spectroscopy (LPSIRS) (Kunimatsu, 1982) and Fourier transform infrared reflection absorption spectroscopy (FT-IRAS) (Kunimatsu, 1987) (IRAS), in which the light beam has to pass through at least  $10^3$  layers of electrolytes before striking the working electrode surface, experiments also showed the presence of these species. No other adsorbed species were detected. Later, Beden et al. (Beden, 1981, 1982 and 1987) claimed an evidence for CHO by EMIRS, although the differential electrochemical mass spectrometry (DEMS) results by Vielstich et al. (Iwasita, 1987) show that there was no CHO as possible adsorbed species in methanol oxidation. Sun et al. (Sun, 1987) applied subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS) in methanol electro-oxidation on Pt (100) in sulfuric acid solution. In addition to the adsorbed CO, they also showed the evolution of CO<sub>2</sub> (band at 2349 cm<sup>-1</sup>) at more positive potentials as product. The other fragments of methanol (CHO, HCHO etc) were also assigned by Christensen in 1988 by using SNIFTIRS investigation (Christensen, 1988). Later, with FT-IRAS measurements, the formation of CO and small amounts of HCHO and HCOOH were obtained during methanol oxidation on Pt (Proenca, 1998, Biegler, 1973).

Although there are extensive studies on the reaction mechanism of the methanol oxidation reaction at Pt electrodes. (Watanabe, 1999; Rauhe, 1995, Biegler and Koch, 1967, Hampson and Willars, 1979) there is some controversy even then, it is possible to construct a probable mechanism for methanol oxidation reaction. Generally, it involves several intermediate steps: CH<sub>3</sub>OH adsorption (Step 1), dehydrogenation (Steps 2 to 4), CO-like species adsorption (Step 5), OH (or H<sub>2</sub>O) species adsorption (Step 6, 7), chemical interaction between adsorbed COH and H<sub>2</sub>O (or OH) (Step 8a) or H<sub>2</sub>O and CO (Step 8b) or OH and CO (Step 8c) to evaluate CO<sub>2</sub>. It has been indicated that Step 8a is the most probable step while step 8b and 8c are the least ones. (Arico, 1996 and 2002, Christensen, 1993; Pletcher, 1982; Chrzanovski, 1998; Ataka, 1996; Osawa, 1997; Beden, 2001; Tapan, 2003; Frelink, 1995).

$$Pt + CH_3OH \rightarrow Pt - (CH_3OH)_{ads}$$
(1)

$$Pt - (CH_3OH)_{ads} \rightarrow Pt - (CH_2OH)_{ads} + H^+ + e^-$$
(2)

$$Pt - (CH_2OH)_{ads} + Pt \rightarrow Pt_2 - (CHOH)_{ads} + H^+ + e^-$$
(3)

$$Pt_2 - (CHOH)_{ads} + Pt \rightarrow Pt_3 - (COH)_{ads} + H^+ + e^-$$
(4)

$$Pt - (COH)_{ads} \rightarrow Pt - (CO)_{ads} + H^{+} + e^{-}$$
(5)

$$Pt + H_2O \rightarrow Pt - (H_2O)_{ads}$$
(6)

$$Pt - (H_2O)_{ads} \rightarrow Pt - (OH)_{ads} + H^+ + e^-$$
(7)

$$Pt_3 - (COH)_{ads} + Pt - (H_2O \text{ or } OH)_{ads} \rightarrow 4Pt + CO_2 + 3H^+ + 3e^-$$
(8a)

$$Pt - (H_2O)_{ads} + Pt - (CO)_{ads} \rightarrow 2Pt + CO_2 + 2H^+ + 2e^-$$
(8b)

$$Pt - (OH)_{ads} + Pt - (CO)_{ads} \rightarrow 2Pt + CO_2 + H^+ + e^-$$
(8c)

It is generally believed that the adsorption of methanol (Steps 1 to 4) on platinum surface occurs between 0.2 V and 0.5 V (vs SHE) and this was verified by both electrochemical and radioactive tracer ( $^{14}$ C) methods. (Kazarinov, 1975). It has been

pointed out that in order to complete methanol oxidation, the oxidation of adsorbed organic fragments,  $Pt_3COH$ , occurs via reaction with a second oxygen containing species,  $H_2O_{ads}$  or  $OH_{ads}$ , which appears at high potentials (0.6 V) (Figure 1. 10).



**Figure 1. 10.** Schematic diagram of methanol oxidation occuring on the surface of a platinum catalyst. Two competing reactions occuring: (a) oxidation of methanol and (b) the poisoning of the platinum catalyst (Gokagac, 1994).

# **1. 5. PERFORMANCE OF PLATINUM-RUTHENIUM METAL CATALYSTS**

In the development of DMFC, the catalysis for the methanol oxidation has been a major challenge. As noted before, PtRu systems are the most active binary catalysts (Adzic, 1979; Watanabe and Motoo, 1975; Hamnett, 1990). Although numerous works have been reported concerning the different aspects of the PtRu catalyst, it remains not fully understood because of its complexity. As stressed in the previous section, active-oxygen-containing surface species are necessary for the oxidative removal of CO-like poisoning intermediates on Pt surfaces (Watanabe, 1975; McNicol, 1977, Arico, 2001). The promotion function of Ru in PtRu catalysts was attributed to the fact that Ru is more active than Pt in terms of promoting water discharge so that the onset potential of the formation of oxygen-containing surface species for Ru is lower than that for Pt (Katayama, 1980; Hamnett and Kennedy, 1988). The optimum composition of PtRu has been a well-studied problem; many works have been devoted to this topic. The answer seems not so straightforward; the optimum percent of Ru in the alloy is a function of working temperature, methanol concentration, and electrode potential (Iwasita, 2000). The situation with nano PtRu catalysts is more complicated than that for the conventionally sized alloys. In recent years, Rolison and co-workers emphasized the importance of hydrous ruthenium oxides, which are highly conductive, both electronically and protonically (Rolison, 1999). In highlighting the function of hydrous oxides, they even denied the necessity of the alloy. However, direct evidence of the promotion function of hydrous oxides has been very limited.

Los Alamos National Laboratory (LANL) constructed a high-performance DMFC using an anode catalyst rich in hydrous ruthenium oxide. Aricò et al (Arico, 1996 and 2002) prepared PtRu catalysts using preformed ruthenium oxides as the supports, but the best performance they obtained was no better than conventionally made PtRu catalysts. Very recently, Spinacé et al. (Spinace, 2004) prepared a catalyst by spontaneous deposition of Pt on carbon-supported Ru nanoparticles and showed good performance for methanol electrooxidation, comparable to that of a commercial

PtRu catalyst. In general, the enhancement of catalytic activity of Pt+second metal catalysts can be explained by : (a) the direct reaction of an oxide of the second metal, such as Ru, with the chemisorbed Pt<sub>3</sub>COH residue, yielding CO<sub>2</sub>. The metal oxide is regenerated via a second redox process (Gokagac, 1994). (b) a blocking effect, in which the second metal, for example Pb, is assumed to inhibit poison formation on the surface of the electrode (Gokagac, 1994) (c) Last, but not least the second metal promotes the formation of active platinum oxide groups capable of completing the oxidation reaction (Gokagac, 1994) Although Pt + Ru is generally taken to be the most active binary catalyst, with increases in methanol oxidation current up to ten times over that of pure platinum, it is noted that many of these bimetallic systems are electrochemically unstable, the second metal dissolving into solution at higher potentials, particularly under potentiodynamic cycling conditions. (Gokagac, 1994; Beden, 1981; Watanabe, 1987; Celik, 2004; Kinoshita. 1977). Therefore, further studies are needed to develop more active PtRu catalysts.

# **1. 6. THE CONCEPT OF NANOPARTICLE**

Nanoparticles are microscopic particles less than 100 nanometers and can be presented as an aerosol (mostly solid or liquid phase in air), a suspension (mostly solid in liquids) or an emulsion (two liquid phases). The principal parameters of nanoparticles are their shape (including aspect ratios where appropriate), size, and the morphological structure of the substance. Both physical and chemical properties for nanoparticles are derived from these principal parameters and desirable compared to the bulk structure. For example, gold nanoparticles melt at much lower temperatures (~300 °C for 2.5 nm size) than the gold plates (1064 °C); and have higher absorption of solar radiation in photovoltaic cells compared to the continuous sheets of this material. It can be summarized that the smaller the particles, the greater the solar absorption. There are also other size-dependent properties such as quantum confinement in semiconductor particles, surface plasmon resonance in some metal particles and superparamagnetism in magnetic materials. However, these properties cannot be always desirable. For instance, the ferromagnetic materials smaller than

10 nm can change their magnetisation direction but this makes them unsuitable for memory storage. Another property of nanoparticles is the high surface area to volume ratio that provides a tremendous driving force for diffusion in different temperatures. The nanoparticles can also have other important properties, for example they can have metallic, semi-sonducting, di-electric, soft, semi-solid character and also have one half hydrophilic and the other half hydrophobic sides that particularly effective for stabilizing emulsions. To get this type of stabilized nanoparticles, there are four main methods; (Hosokowa, 2007, Roucoux, 2002).

- Electrostatic stabilization
- Steric stabilization
- Electrosteric stabilization
- Ligand or surfactant stabilization

In electrostatic stabilization, finely distributed particles can be stabilized by utilizing the ionic species such as halides or carboxylates. There is a generation of double layer resulting in confined particles by the ionic compounds owing to Coulombic repulsion between nanoparticles as shown in Figure 1. 11.



**Figure 1. 11.** Schematic representation of electrostatic stabilization (http://wikis.lib.ncsu.edu/index.php/Nanoparticles, May 4, 2008)

In the steric stabilization, the adsorption of surfactants (polymers or oligomers) creates a protective layer which keeps the nano-sized particles away from each other. In addition to that, the length and nature of the surfactant has an effect on nanoparticles (Figure 1. 12).



**Figure 1. 12.** Schematic representation of steric stabilization http://depts.washington.edu/solgel/images/courses/MSE\_502/Ch\_2/figure\_2.22.JPG

In the electrosteric stabilization, more complex surfactants, a polar head to surround the particle and lypophilic tail provides steric repulsion in solvent, are used to maintain the stability of metal particles (Figure 1. 13).



**Figure 1. 13.** Schematic representation of electrosteric stabilization (Roucoux et al, 2002)

Lastly, ligand stabilization is used for stabilizing the transition metal colloids by protecting them from aggregation (using ligands such as thiols or amines). (Ertan, 2011) as shown in Figure 1. 14.



Figure 1. 14. Schematic representation of ligand stabilization (Sen et al, 2007)

In this thesis, ligand or surfactant stabilization method was used to obtain carbon supported Pt and PtRu catalysts. Generally, surfactants are organic compounds which are used to lower the surface tension of a liquid. These surfactants contain both hydrophobic and hydrophilic group. Hydrophobic group is repelled by water which means it does not like water and hydrophilic group are attracted towards water and tend to dissolve in water. Surfactants can be classified based on charged groups present in their head as:

- a) Anionic surfactants
- b) Nonionic surfactants
- c) Cationic surfactants
- d) Amphoteric/Zwitterionic surfactants

#### a) Anionic Surfactants

These types of surfactants are dissociated in water in an amphiphilic anion and a cation which is in general an alkaline metal ( $Na^+$ ,  $K^+$ ) or a quaternary ammonium. They are the most commonly used surfactants and most of the anionic surfactants are carboxylate, sulfate and sulfonate ions. There are five subgroups of anionic surfactants;

- alkali metal soaps which are sodium, potassium or ammonium salts of long chain fatty acids such as oleic, stearic and ricinoleic acid,
- divalent and trivalent metal soaps that are less alkaline and less sensitive to acids,
- amine soaps in which triethanolamine surfactant is preferentially used for pharmaceutical applications,
- alkyl sulphates and alkyl phosphate that are the esters of fatty alcohols and sulphuric acids. Most widely used surfactants from alkyl sulphates are sodium lauryl sulphate.

## b) Nonionic Surfactants

These surfactants do not have any electrical charge, which means that they do not ionize in aqueous solution, such as thiol, alcohol, phenol, ether, ester, or amide. They are second most widely used surfactants with about 45 % of the overall industrial production. If we compare those with other types of surfactants and it can be said that they are less irritant than other anionic or cationic surfactants. Generally, in this type of surfactants, while the hydrophilic part contains the polyoxyethylene, polyoxypropylene or polyol derivatives, the hydrophobic part contains saturated or unsaturated fatty acids or fatty alcohols. The most commonly used non-ionic surfactants are ethers of fatty alcohols.

The non ionic surfactant can be classified as

i) polyol esters that includes glycol and glycerol esters and sorbitan derivatives,ii) polyoxyethylene esters that contains polyethylene glycol (PEG 40, PEG -50, PEG-55),

iii) poloxamers

# c) Cationic Surfactants

Those surfactants are dissociated in water into an amphiphilic cation and an anion, such as fatty amine salts and quaternary ammoniums, with one or several long chain of the alkyl type. In solution, their head is positively charged. They are mostly used for their disinfectant and preservative properties as they have good bactericidal properties. Mostly used cationic surfactants are cetrimide which has tetradecyl trimethyl ammonium bromide with minimum amount of dodecyl and hexadecyl compounds. Other cationic surfactants are benzalkonium chloride, cetylpyridinium chloride etc. These surfactants are in general more expensive than anionics, due to the high pressure hydrogenation reaction to be carried out during their synthesis.

#### (d) Amphoteric/Zwitterionic Surfactants:

These surfactants can be negatively, positively or no charged in solution, depending on the acidity or pH of the water. They may also contain two charged groups of different sign at the same time. Generally, the positive charge of the surfactants is almost always ammonium but the negative charge may vary such as carboxylate, sulphate, sulphonate. They are frequently used in shampoos and other cosmetic products because of their high foaming and excellent dermatological properties (Rosen, 2012).

Generaly, there are lots of applications for the anionic, cationic, non-ionic and amphoteric/zwitterionic surfactants such as, they

- are used in many cleaning and hygienic products like floor cleaner, detergents, dish washer, car wash soaps, toothpastes, shampoos, shaving foams and bubble bath formulations.
- also work as foaming agent which can form foam in any substance easily.
- o also used as an antiseptic in many personal sanitary products.
- are used in paints, adhesives, inks, emulsions etc.
- are also used in the preparation of micelles especially in the nanocatalyst preparation to prevent agglomeration

The widespread applications of surfactants in pratical applications and scientific interest in their nature and properties, have precipitated a wealth of published literature on the subject (Hui, 2005; Duy, 2010, Tong, 2005). Although surfactant science is now a reasonably mature discipline, there is still room for new molecules designed for specific purposes and new applications such as nanoparticle synthesis and more diverse and environmentally friendly consumer products. To prepare such type of nanoparticle, different types of surfactants have been utilized. For example, Hui et al (Hui, 2005) prepared Pt particle that has 2.2 nm particle size using 3 (N-N dimethyldodecylammonio) propanosulfonate (SB12) as surfactant. Duy et al (Duy, 2010) synthesized gold nanoparticles using tween 20 (polyoxyethylene (20) sorbitan monolaurate) molecules as surfactant. Similarly, Tong et al (Tong, 2005), Isaacs et al (Isaacs, 2006), Tu et al (Tu, 2003) and Brust et al (Brust, 1994) synthesized different kinds of Pt nanoparticles using octanethiol, decanethiol, dodecanethiol and hexanethiol as surfactants, respectively. It has been found that types of surfactants, the chain length, presence of charged functional group and packing density of the

surfactants, play an important role on the size of the metal nanoparticles. For instance, ~ 1.5, 2.0, 1.9, 1.8, 2.2, 1.5, 1.0 and 4 nm diameter platinum nanoparticles have been produced using 4-mercaptoaniline (Yee, 1999), octanethiol (Tong, 2005; Ertan, 2012), decanethiol (Isaacs, 2006; Ertan, 2012), heptanethiol (Sen, 2011), 1,1 dimethyl heptanethiol (Sen, 2011), hexadecanethiol (Sen, 2011), octadecanethiol (Perez, 1999, Sen, 2011) and dodecanethiol (Tu, 2003; Ertan, 2012) surfactants, respectively. However, the branched surfactants like tert-octanethiol have never tried to prepare this type of nanocatalysts. For this purpose, in this thesis, hexanethiol and tert-octanethiol were used as surfactants to get carbon supported Pt and PtRu catalysts and prepared catalysts were compared in terms of catalytic activity, size etc.

#### **1.7. THE OBJECTIVE OF THE WORK**

As stressed at the beginning of this chapter, fuel cells are very attractive electrochemical devices, which convert the chemical energy of the fuel directly into electrical energy, because they are cleaner and more efficient energy sources compared to the fossil fuels. Direct methanol fuel cells (DMFC) are one of the most important ones since methanol is liquid at room temperature, so it can be directly used in the fuel cells without any storage or transportation problems. The main problem for DMFC is the poor electrochemical activity of methanol which prevent practical applications. In order to activate methanol, enormous studies have been performed, however, no such active catalysts have been found. The important parameter in these catalysts is the active surface area. The greater the active surface area is the greater the performance of the catalyst. Thus, in order to increase the active surface area of the catalyst, the particle size of the catalyst should be decreased to the nanometer scale. Therefore, in this thesis, firstly, platinum nanoparticles have been prepared using PtCl<sub>4</sub> and H<sub>2</sub>PtCl<sub>6</sub> as starting materials, 1-hexanethiol and tertoctanethiol as surfactants by using optimized chemical reduction method in order to see the effect of different types of surfactant on catalytic performance. Then, the activity of these catalysts have been determined by electrochemical cell method like cyclic voltammetry (CV) toward methanol oxidation reaction. These catalysts were also characterized by following techniques a) Transmission Electron Microscopy (TEM) b) Energy Dispersive Analysis (EDS) c) X-ray Photoelectron Spectroscopy (XPS) d) X-Ray Diffraction (XRD) e) Fourier Transform Infrared Spectroscopy (FTIR). Secondly, the prepared catalysts were heated at the different temperatures, (200, 300, 400 °C) under inert atmosphere in order to observe the effect of heat on the performance of the catalysts. These heat-treated catalysts were also characterized by above techniques. Lastly, in order to define the effect of Ru as a second metal and to find out the optimum Pt to Ru ratio on the activity of the catalyst, Ru was added to Pt nanoparticles in different ratios and they were characterized by the same techniques and examined toward methanol oxidation reaction by electrochemical techniques.

# **CHAPTER 2**

# **EXPERIMENTAL**

#### 2. 1. SYNTHESIS OF Pt CATALYSTS

## 2.1. 1. SYNTHESIS OF THE CATALYST I

1.0 mmol (0.3371g) of PtCl<sub>4</sub> (99 % Alfa) was dissolved by stirring vigorously in 20 ml of anhydrous tetrahydrofuran (THF, 99.5%, Merck). Then 1.0 mmol (149  $\mu$ L) of 1-hexanethiol was added to this solution and the mixture was stirred vigorously for 2.5 hours. Finally, the thiol stabilized platinum complex was reduced by drop wise addition of lithium triethylborohydride (superhydride, 1.0 M dissolved in THF, Aldrich). Superhydride addition was continued until no H<sub>2</sub> gas bubbled from the solution, indicating a complete reaction (Equation 2.1). All of these steps were performed under high-purity argon atmosphere. The observation of a reddish-brown color to the solution indicated the formation of platinum nanoparticles. In order to remove the surfactant from the reaction medium, the resulting solution was washed with copious amount of dry ethanol (99.9 %, Merck). Finally, the solid residue was dried under vacuum at room temperature.

 $PtCl_4-surfactant + 4LiBEt_3H \rightarrow Pt(nanoparticles)-surfactant + 4BEt_3 + 4LiCl + 2H_2\uparrow (2.1)$ 

#### 2.1. 2. SYNTHESIS OF CATALYSTS II, III, IV

Catalysts II, III and IV were prepared in an identical manner using an appropriate amount of  $H_2PtCl_6$  and 1-hexanethiol;  $PtCl_4$  and tert-octanethiol; and  $H_2PtCl_6$  and

tert-octanethiol, respectively, Table 2.1. Lithium triethylborohydride was used as a reducing agent for all syntheses.

Catalysts	Platinum complexes	Surfactant
Catalyst I	PtCl <sub>4</sub>	1-hexanethiol
Catalyst II	$H_2PtCl_6$	1-hexanethiol
Catalyst III	PtCl <sub>4</sub>	Tert-octanethiol
Catalyst IV	$H_2PtCl_6$	Tert-octanethiol

Table 2.1. Platinum complexes and surfactant used for all the prepared catalysts.

# 2. 2. HEAT-TREATMENT EXPERIMENTS FOR CATALYSTS I AND II

The stabilizing surfactant shell around the metal nanoparticles had to be removed before they could be used as electrocatalysts (Liu, 2004), because platinum acts as a main catalyst towards methanol electrooxidation reaction. For this purpose, synthesized carbon supported surfactant stabilized Pt nanoparticle catalysts as shown in Table 2. 2 were heat-treated under argon atmosphere at different temperatures (between 200 to  $400^{\circ}$  C by rising  $100^{\circ}$  C in each step) for 4h in order to define the optimum heating temperature for high performance of methanol electrooxidation reaction.

Catalysts	Platinum complexes	Surfactant	Heat (°C)-Time (h)
Catalyst Ia	PtCl <sub>4</sub>	1-hexanethiol	200 - 4
Catalyst IIa	$H_2PtCl_6$	1-hexanethiol	200 - 4
Catalyst Ib	PtCl <sub>4</sub>	1-hexanethiol	300 - 4
Catalyst IIb	$H_2PtCl_6$	1-hexanethiol	300 - 4
Catalyst Ic	PtCl <sub>4</sub>	1-hexanethiol	400 - 4
Catalyst IIc	$H_2PtCl_6$	1-hexanethiol	400 -4

Table 2. 2. Platinum complexes and surfactant used for all the prepared catalysts.

## 2. 3. SYNTHESIS OF Ru CATALYST

Appropriate amount of  $RuCl_3$  (Sigma) and 1-hexanethiol were used as a starting material and surfactant, respectively and the same procedure was followed as in Section 2.1.1. In this case, the observation of dark brown solution instead of reddish brown indicated the formation of ruthenium nanoparticles.

# 2. 4. SYNTHESIS OF BIMETALLIC Pt-Ru CATALYSTS

#### 2.4. 1. SYNTHESIS OF CATALYST A (70% Pt + 30% Ru)

A 0.34 mmol (0.071 g) of RuCl<sub>3</sub> were dissolved in 20 ml of anhydrous tetrahydrofuran and left for an hour. Then, 0.34 mmol (68.5  $\mu$ L) of tert-octanethiol surfactant (C<sub>8</sub>H<sub>18</sub>SH, 95 %, Merck) was added to the ruthenium solution and this mixture was stirred vigorously for 2.5 hours. Next, thiol stabilized RuCl<sub>3</sub> complex was reduced by dropwise addition of lithium triethylborohydride. Afterwards, appropriate amount of PtCl<sub>4</sub> solution (70% Pt + 30% Ru) was added to this mixture

and superhydride addition was continued until no  $H_2$  gas bubbled from the solution. All of these steps were performed under high-purity argon atmosphere. The excess thiols in the reaction medium were removed by ethanol. The solid residue which was produced was dried under vacuum at room temperature and finally the prepared metal nanoparticles were mixed in a 1:10 ratio with carbon XC-72 which was used as a support.

# 2.4. 2. SYNTHESIS OF CATALYSTS B and C

Catalysts B (80% Pt + 20% Ru) and C (90% Pt + 10% Ru) were prepared in an identical manner in Section 2.4. 1 using an appropriate amount of PtCl<sub>4</sub>, RuCl<sub>3</sub> and tert-octanethiol as shown in Table 2. 3. Lithium triethylborohydride was used as a reducing agent for all syntheses.

**Table 2. 3.** Platinum and Ruthenium complexes, surfactant used for all the prepared catalysts.

Catalysts	Platinum and Ruthenium complexes	Surfactant	Pt/Ru ratio
Catalyst A	PtCl <sub>4</sub> - RuCl <sub>3</sub>	Tert-octanethiol	70% Pt + 30% Ru
Catalyst B	PtCl <sub>4</sub> - RuCl <sub>3</sub>	Tert-octanethiol	80% Pt + 20% Ru
Catalyst C	$PtCl_4 - RuCl_3$	Tert-octanethiol	90% Pt + 10% Ru

# **2. 5. PREPARATION OF CARBON SUPPORTED METAL (Pt and Pt/Ru)** NANOPARTICLE CATALYSTS

As synthesized Pt or PtRu nanoparticle catalyst was mixed with Cabot Vulcan XC-72 carbon (10 wt % nanoparticle) (Liu, 2004) and 10 ml of dry ethanol was added to the mixture and it was stirred vigorously overnight in order to obtain uniform distribution of metal nanoparticles on carbon support. Finally, the solid residue was dried at room temperature under vacuum.

# 2. 6. ELECTRODE PREPARATION FOR NANOPARTICLE CATALYSTS

The electrode solution was prepared by mixing 36.78 mg of prepared carbon supported powder catalyst, 0.5 ml of Nafion (Aldrich, 5 wt %), 0.15 ml of N,N-dimethyl formamide (Merck, 99.5 %) and 2.5 ml of distilled water. The heterogeneous mixture was sonicated until almost homogenous dispersion of solid in solution was obtained. 50  $\mu$ l of the slurry solution was dropped on the 0.7 cm diameter of glassy carbon which was used as a working electrode. To complete the preparation of the working electrode, drying process was applied by heating the electrode from 40  $^{\circ}$ C (20 min.) to 65  $^{\circ}$ C (20 min.) and finally to 100  $^{\circ}$ C (60 min.) gradually to get good adhesion. (Gökağaç, 2003).

# 2. 7. ELECTROCHEMICAL CELL

Execution of cyclic voltammetry measurements were hold by the use of a microcomputer-controlled potentiostat/galvanostat, Solartron 1285, at room temperature (Department of Chemistry, METU). The working electrode was made up of catalysts settled on a 0.7 cm diameter glassy carbon. The saturated calomel electrode (SCE), glassy carbon and prepared catalysts were used as a reference,

counter and working electrodes, respectively. 0.1 M HClO<sub>4</sub> (60 %, Merck) + 0.5 M CH<sub>3</sub>OH (99.9 %) solutions were utilized as an electrolyte as shown in Figure 2. 1.

In order to remove the oxygen in the electrolyte and in the cell, pure argon was passed through the electrolyte for fifteen minutes before the measurements were taken.



Figure 2. 1. An electrochemical cell

# 2. 8. CHARACTERIZATION TECHNIQUES

# 2.8. 1. DETERMINATION OF METAL CONTENTS IN SYNTHESIZED NANOPARTICLE CATALYSTS

A certain amount of as synthesized carbon supported Pt or Pt-Ru nanoparticle catalyst was burned at high temperature in a porcelain dish using bunsen burner in order to remove carbon and unremoved surfactant content of catalyst, but metal. 100 ml of aqua regia [the mixture of 3 volumes of HCl (37 %, Merck) and one volume of  $HNO_3$  (65 %, Merck)] was added to solid residue in order to dissolve metals. The mixture was then evaporated until the volume decreased to 25 ml and 25 ml of concentrated HCl was added to the solution. This process was repeated 4 times. Finally, the resulting solution was filtered and diluted to 100 ml with distilled water. The metal content of catalyst was determined by ICP-OES (Leeman Labs, Inc.).

#### 2.8. 2. CYCLIC VOLTAMMETRY (CV)

Cyclic voltammetry (CV) is the one of the most important electrochemical techniques which measures the current that develops in an electrochemical cell. CV can be used as an identification tool about electrochemical processes under various conditions, such as the presence of intermediates in redox reactions, the reversibility of a reaction, determination of the electron stoichiometry of a system, the diffusion coefficient of an analyte, and the formal reduction potential. In addition, since concentration is proportional to current in a reversible, Nernstian system, concentration of an unknown solution can be determined by generating a calibration curve of current vs. concentration.

In cyclic voltammetry, the scientists generally use three electrodes system that refers to the reference, working and counter electrodes. In this system, the potential is applied between the reference electrode and the working electrode and the current is measured between the working electrode and the counter electrode and then data can be plotted as current (*i*) vs. potential (*E*). As clearly shown in Figure 2. 2, CV measurements are executed by implementing a repetitive triangular potential excitation signal which results in a sweep back and forth between two switching potentials on working electrode's potential (Scholz, 2002).

The main working principle of this technique depends on the variation of the applied potential exerted on a working electrode in both forward and backward scans. In typical cyclic voltammetry, electron transfer is driven by the surface's adequate positivity or negativity in voltage which caused by the oxidation or reduction of the solution component by the touch of the solution with the electrode surface. In simple cases, a particular voltage is exerted on the surface at the beginning with respect to a reference and the electrode voltage is varied linearly in both forward and backward scans. Due to this variation in voltage, surface becomes adequately positive or negative through which electron transfer takes place between the chemical species and the surface. This gives rise to a measurable current in the circuit. As a result of the reversed voltage cycle, electron transfer is also reversed, resulting in an inverse current peak. Depending on the analysis, one full cycle, a partial cycle, or a series of cycles can be executed and the current at the working electrode is measured through the potential scan so as to acquire a cyclic voltammogram. A typical cyclic voltammogram showing the reduction and oxidation current peaks is given in Figure 2. 3 (Kissinger, 1996).

In this thesis, as electrochemical techniques, cyclic voltammetry (CV) was utilized by using a microcomputer-controlled potentiostat/galvanostat, Solartron 1285, at room temperature. The reference, counter and working electrodes were assigned as the saturated calomel electrode (SCE), glassy carbon and prepared catalysts respectively (Department of Chemistry, METU).



Figure 2. 2. Typical excitation signal for cyclic voltammetry.

(http://www.earlham.edu/~chem/chem341/c341\_labs\_web/cyclic\_voltammetry.pdf)



**Figure 2. 3.** A typical cyclic voltammogram displaying reduction and oxidation current peaks.

# 2.8. 3. X-RAY DIFFRACTION

X-ray diffraction is a very powerful, analytical and nondestructive method used for the examination of fingerprint characterization and structure determination. X-ray diffraction is used for the determination of the actual arrangement of atoms within a crystalline specimen. The relationship describing the angle at which a beam of Xrays of a particular wavelength diffracts from a crystalline surface was discovered by Sir William H. Bragg and Sir W. Lawrence Bragg and is known as Bragg's Law. The diffraction peak appears under certain conditions satisfying the Bragg condition:

#### $2d\sin\theta = n\lambda$

where;  $\lambda$ ,  $\theta$ , n and d are wavelength of the x-ray, the Bragg angle at where diffraction peak is observed, an integer representing the order of the diffraction peak and the distance between atomic planes, respectively (He, 2009; Warren, 1990), Figure 2. 4.



Figure 2. 4. The incident and scattered X-rays.

Two major X-ray techniques is available for X-ray diffraction namely, single crystal and powder methods. Single crystal X-ray diffraction is a technique used to determine the structure of crystalline materials including inorganic compounds and complex macromolecules like proteins or polymers. Single crystal is required to discover the nature of the crystal structure.

Single crystal X-ray crystallography plays a crucial role in terms of the determination of molecular conformations of biological species; however, acquisition of a single crystal is so tough. In addition to this, this method offers advantages that diffraction peaks from only the selected crystal plane are observed which makes the characterization easier.

On the other hand, powder X-ray diffraction is applied for the characterization of crystallographic structure, grain size, and preferred orientation in polycrystalline or powder solid samples. Unknown crystalline materials can be analyzed by the help of this method in terms of making comparison of the diffraction data of the compounds with the database (International Centre for Diffraction Data (ICDD)) of the known materials.

As pointed out earlier in this section, X-ray diffraction is a powerful tool to employ not only for the fingerprint characterization but also for the structure and size determination. In this study, the average particle sizes of the prepared catalysts were calculated from the X-ray diffraction pattern by using Scherrer formula (Klug, 1962):

$$d\left(\mathrm{\AA}\right) = \frac{k\lambda}{\beta \cos\theta}$$

where d is the average particle size, k is a coefficient (0.9),  $\lambda$  is the wavelength of Xray (1.54056 Å),  $\beta$  is the full width half-maximum of respective diffraction peak (rad) and  $\theta$  is the angle at the position of peak maximum (rad). Rigaku diffractometer with Ultima + theta-theta high resolution goniometer, the X-ray generator (Cu K $\alpha$ radiation,  $\lambda = 1.54056$ Å) with operation conditions at 40 kV and 40 mA were employed for the X-ray diffraction analysis (Central Lab., METU).

# 2.8. 4. TRANSMISSION ELECTRON MICROSCOPY (TEM) AND ENERGY DISPERSIVE X-RAY SPECTROSCOPY (EDS)

Transmission Electron Microscopy (TEM) is a well known and widely used microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen. A TEM uses electrons instead of visible light in light microscope, due to the smaller wavelength of electrons compared to the visible light. A TEM uses magnetic lenses to deflect electrons instead of glass lenses. This microscope is very similar to a conventional microscope, complete with condenser, objective and projector lenses as shown in Figure 2. 5.

Electrons are collimated from the source, passed through the sample, and the resulting pattern is typically recorded with a CCD camera. This pattern can be used to map of the material's density in thin samples. The lateral resolution is achieved for a resolution of 0.2 nm by the use of much smaller wavelength of electrons.

Image contrast is acquired by the interaction between the electron beam and the sample and the areas having high density and having heavier elements seem darker in a TEM image owing to the scattering of the electrons in the sample. Scattering from crystal planes also creates diffraction contrast that is presumably dependent on the orientation of a crystalline area in the sample. As a result, each crystal possesses its own grey-level which helps one to differentiate not only materials but also individual crystals and crystal defects in a sample having randomly oriented crystals. Atomic arrangements in crystalline structures can be examined in a detailed way by TEM due to its high resolution.

The first step in phase identification is a chemical analysis that can be done in a TEM microscope by *X-rays energy dispersive spectrometry*, EDS. The interaction between the incident electron beam and the sample evoke the emission of X-rays. The energies of the X-rays are specific for the atoms present in the volume that is probed. Energy dispersive X-ray analysis is the name given to the detection and characterization of the X-rays. The elemental composition can be acquired by the X-

ray spectrum in the irradiated area. an X-ray spectrum is acquired from small regions of the specimen illuminated with a focused electron beam, usually using a solid-state detector. Characteristic X-rays from the chemical elements are used to determine the concentrations of the different elements in the specimen (Carter, 2009).

JEOL 200 kV TEM instrument was used to acquire transmission electron microscopy (TEM) images. Sample preparation for TEM analysis involved dispersion of carbon supported catalyst in ethanol by the use of ultrasonic bath and then placement of a drop of (~0.5 mg/mL) this solution on a carbon covered 400-mesh copper grid and the solvent was evaporated before TEM analysis (Central Lab., METU).



Figure 2. 5. Block diagram of typical TEM (Transmission Electron Microscopy).

# 2.8. 5. X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

X-ray Photoelectron Spectroscopy (XPS) is quantitative spectroscopic technique that determines the elemental composition (for top 1-10 nm particles usually), empirical formula, chemical state and electronic state of the elements that exist within a material. X-ray photoelectron spectroscopy (called variously XPS or ESCA - electron spectroscopy for chemical analysis), employing X-ray radiation as the ionizing source, has been largely concerned with the ejection of core electrons as shown in Figure 2. 6.



Figure 2. 6. The energies of electrons ejected from core levels in X-ray photoelectron spectroscopy (XPS).

The energy, required to liberate an electron from a system, using the vacuum as a reference level,  $E_{b}$ , can be calculated from a consideration of energy conversation:

 $E_b = E_{source}$  -  $E_{kin}$  -  $E_r$ 

where  $E_{source}$  is the energy of the ionizing radiation,  $E_{kin}$  is the kinetic energy of the photoelectron, and  $E_r$  is the recoil energy of the atom or molecule. A photoelectron spectrum is thus a plot of the number of photoelectrons incident upon a suitable counting device as a function of the kinetic energy of the photoelectrons.

The usual sources of X-rays are Mg K $\alpha$  (1253.6 eV) or Al K $\alpha$  (1486.6 eV). Since the energies of atomic core levels are characteristic of each element, XPS can be used to obtain the relative amount of elements on the surface of the sample. The ionization potential of atomic core level depends to some extend on the chemical environment of the atom, so that information can also be obtained around the type of bonding between adsorbate and the surface and oxidation state of each element (Watts, 2003).

In this study, the binding energies of Pt  $4f_{7/2}$  and  $4f_{5/2}$ , Ru  $3p_{3/2}$  and Ru  $3p_{1/2}$ , S  $2p_{3/2}$ , S  $2p_{1/2}$  and C1s electrons were determined for synthesized Pt, Ru and PtRu nanoparticle catalysts by Specs spectrometer using K $\alpha$  lines of Mg (1253.6 eV, 10 mA) as a X-ray source. The spectrometer has two stainless steel chambers with independent pumping systems. The first chamber is a fast entry lock working between  $10^{-4}$ - $10^{-5}$  torr. The second chamber operates between  $10^{-9}$ - $10^{-10}$  torr and is used to remove high volatile gases. The second chamber is the main chamber where the spectroscopic values are taken by a hemispherical analyser with a multichannel detector. The Ar<sup>+</sup> ion flood was used to clean the surface when necessary. Samples were held in a cupper holder with double-sided tape. All lines were referenced to the C 1s line at 284.6 eV. Peak fittings of Pt and Ru and S regions of nanoparticle catalysts were done using Kaleidagraph fit programme.

#### 2.8. 6. FT-IR (Fourier Transform InfraRed) Spectroscopy

FT-IR spectroscopy is a technique for materials analysis in the laboratory. In this spectroscopy, infrared light is passed through a sample. As shown in Figure 2. 7, some of the infrared source is absorbed by the sample and some of it is transmitted. The resulting spectrum represents the frequencies of vibrations between the bonds of

the atoms making up the material. Each different material produce the different infrared spectrum. Therefore, infrared spectroscopy can be used for qualitative and quantitative analysis (by using the size of the peaks in the spectrum). (Griffiths, 2007).



Figure 2. 7. Working principle of FTIR spectroscopy

The first kind of infrared instruments were the dispersive type. Generally, these type of instruments have an infrared source, mirrors, chopper, grating and detector as shown in Figure 1. 15. Infrared source is sent through both a reference and sample path, through a chopper that moderates the energy reaching the detector, and directs to a diffraction grating. This grating works like prism that separates visible light into its frequencies. The detector measures the amount of energy at each frequency which has passed through the sample. This results in a plot of intensity vs. frequency.



Figure 2.8. Dispersive spectrometer diagram

Because dispersive types of IR has lots of limitations like slow scanning process etc, the introduction of FTIR spectrometry can be accepted as the most significant advances in infrared spectroscopy. FTIR spectrometry has a capability of the measuring all of the infrared frequencies simultaneously, rather than individually by using a very simple optical device called an interferometer. This device produces very quickly a unique type of signal which has all of the infrared frequencies "encoded" into it. This takes just on the order of one second or so. Therefore, the signal time per sample is just a few seconds rather than several minutes. The resulting signal is called an interferogram in which all frequencies are being measured at the same time. Since the analyst requires a plot of the intensity at each individual frequency in order to identify the structure of the molecule, the measured interferogram signal can be interpreted directly via a well-known mathematical technique called the FT (Fourier transformation). This transformation is performed by the computer which presents the user with the desired spectral information for analysis (Banwell, 1994). As a summary, the normal instrumental process composed of the followings (Figure 2.8):

**1. The Infrared Source:** is emitted from a glowing black-body source.

**2. The Interferometer:** The beam enters the interferometer where the "spectral encoding" takes place.

**3. The Sample:** The beam is transmitted through or reflected off of the surface of the sample, depending on the type of analysis.

4. The Detector: The beam finally passes to the detector for final measurement.

**5. The Computer:** The measured signal is digitized and sent to the computer where the Fourier transformation takes place.

Some of the major advantages of FT-IR over the dispersive technique can be summarized as:

• **Speed:** Since all frequencies are measured at the same time, FT-IR measurements just take on the order of a second rather than several minutes.

• Sensitivity: Since The FTIR detectors are much more sensitive, have higher signal to noise ratio, and the fast scans, FT-IR spectrometry improved the sensitivity dramatically.

• **Mechanical Simplicity:** Because there is just one moving part in the instrument, (moving mirror), mechanical breakdown is very difficult.

• **Internally Calibrated:** These instruments are self-calibrating and no need to be calibrated by the user. A HeNe laser is used as an internal wavelength calibration standard.



Figure 2. 9. Block diagram of FT-IR spectroscopy

These advantages, along with several others, make measurements made by FT-IR extremely accurate and reproducible. (Prati, 2010). Because there needs to be a relative scale for the absorption intensity, a background spectrum, that is normally a measurement with no sample in the beam, must also be measured. This can be compared to the measurement with the sample in the beam to determine the "percent

transmittance." In this thesis, FTIR spectra were recorded on a Bruker 66 v/s at room temperature using KBr pellets with 100 scans.

#### **CHAPTER 3**

# **RESULTS AND DISCUSSIONS**

3. 1. CHARACTERIZATION AND ELECTROCHEMICAL STUDIES FOR CATALYST I (PtCl<sub>4</sub> + 1-Hexanethiol), CATALYST II (H<sub>2</sub>PtCl<sub>6</sub> + 1-Hexanethiol), CATALYST III (PtCl<sub>4</sub> + Tert-Octanethiol) AND CATALYST IV (H<sub>2</sub>PtCl<sub>6</sub> + Tert-Octanethiol)

# 3.1. 1. X-RAY DIFFRACTION (XRD) AND TRANSMISSION ELECTRON MICROSCOPY (TEM) OF CATALYSTS I, II, III AND IV

The analysis of the crystalline structure and particle size of the platinum nanoparticles were performed by using X-ray diffraction (XRD) and transmission electron microscopy (TEM). The powder diffraction patterns of all catalysts showed broad peaks  $2\theta = 39.90$ , 46.20, 67.40 and 81.50 which was assigned to Miller indices (111), (200), (220) and (311) for the planes of the face-centered cubic (fcc) crystal lattice of platinum (Figure 3. 1). The line broadening was a result of the small size of the particles. Additional peaks were also observed in the diffraction pattern at  $2\theta = 21.35$ , 23.15, 30.55 and 31.65. In order to explain these peaks, when the XRD spectrum of only superhydride is examined, it is thought that these peaks can be attributed to the superhydride crystals which could not be removed during cleaning process (Figure 3. 1).

From full width half maximum of the (220) peaks in XRD, the average crystallite platinum particle size of all the catalysts was calculated using Scherrer equation (Klug, 1962), Table 3. 1;

$$d(\text{\AA}) = \frac{k\lambda}{\beta cos\theta}$$

where,

d= Pt particle size

k= a coefficient (0.9)

 $\lambda$ = the wavelength of X-ray used (1.54056 Å)

 $\beta$ = the full width half-maximum of respective diffraction peak (rad)

 $\theta$ = the angle at the position of peak maximum (rad)

The average particle size of the platinum Catalyst I and II was found to be about 2 nm. This is in agreement with the results of Eklund and Cliffel (Eklund, 2004). They synthesized platinum nanoparticles starting with  $H_2PtCl_6.6H_2O$  and using hexanethiol and tiopronin as surfactants. The particle size is not dependent on the type of platinum precursor complex used. The average platinum particle size of Catalysts III and IV was larger than Catalysts I and II, about 3 nm. It is thought that an increase in the particle size might be due to the branched structure of the tert-octanethiol. A more branched surfactant may have a tendency to form a larger hole in the micelles which in turn would cause an increase in the particle size of the metal which forms in the cavity of micelle. A schematic representation of this idea is given in Figure 3. 2.


Figure 3. 1. X-ray diffractograms of blank, Catalyst I, II, III and IV.

**Table 3. 1.** Average crystallite platinum particles size determined by a) X-ray line broadening and b) transmission electron microscopy.

Samples	a (nm)	b (nm)
Catalyst I	~ 2.00	~ 2.00
Catalyst II	~ 2.13	~ 2.00
Catalyst III	~ 2.95	~ 3.00
Catalyst IV	~ 2.85	~ 3.00



Figure 3. 2. A schematic representation of formation of the platinum nanoparticles.

In order to solidify the results of diffraction measurements, transmission electron microscopy was used. The high resolution transmission electron micrograph which is a representative of morphology of the other prepared catalysts as well and particle size histogram of the catalyst I are given in Figure 3. 3 and 3. 5a, respectively. A relatively narrow range of platinum particle sizes and uniform distribution of those nanoparticles on the carbon support was observed by this technique. The average particle size was found to be about  $2 \pm 0.3$  nm which agrees with the XRD data. Transmission electron micrographs of powder samples of Catalyst II showed the platinum particle size and distribution to be similar to Catalyst I. Figure 3. 4 and 3. 5b show that Catalyst III has a size of about 3 nm in diameter, also agreeing with the XRD data, and a uniform distribution on the carbon support. The transmission electron micrograph of Catalyst IV was identical to Catalyst III. In all cases, there is no evidence of agglomeration of the platinum nanoparticles.



Figure 3. 3. Transmission electron micrograph of Catalyst I.



Figure 3. 4. Transmission electron micrograph of Catalyst III.



**Figure 3. 5.** The histogram of the platinum particle size distribution of catalysts I (a) and III (b).

# 3.1. 2. FTIR SPECTRUM OF CATALYST I, II, III AND IV

The FTIR spectra of 1-hexanethiol, *tert*-octanethiol, carbon XC-72, and catalysts I-IV (KBr pellets) are shown in Figure 3. 6. The FTIR spectra of monomeric 1hexanethiol and *tert*-octanethiol indicate the symmetric and asymmetric  $CH_2$ stretching of  $CH_2$  and  $CH_3$  groups in the chain between 2800 and 3000 cm<sup>-1</sup>, a S-H stretching band at about 2560 cm<sup>-1</sup>, a  $CH_2$  scissoring band between 1500 and 1430 cm<sup>-1</sup>, and the twisting of  $CH_2$  groups, symmetric and asymmetric stretching of C-C-C bonds, wagging of  $CH_3$  and twisting of SH, and rocking and torsion of  $CH_2$  were observed at lower than 1400 cm<sup>-1</sup> (Hostetler et al, 1996; Nuzzo et al, 1990).

To investigate the species around the platinum nanoparticles, FTIR spectra of catalysts I-IV before the addition of carbon XC-72 and carbon XC-72 itself were measured as shown in Figure 3.6. c-g. The spectra of all samples showed quite similar patterns. A symmetric and asymmetric CH<sub>2</sub> stretching of CH<sub>2</sub> and CH<sub>3</sub> are observed between 2800 and 3000 cm<sup>-1</sup>, as seen in monomeric 1-hexanethiol and tertoctanethiol. A new peak is observed at about 2498 cm<sup>-1</sup> next to the S-H stretching band at 2560 cm<sup>-1</sup>, which might be attributable to the presence of a C=O group. Quite strong bands are seen for the scissoring of CH<sub>2</sub> groups between 1600 and 1350 cm<sup>-1</sup> and a sharp band for the rocking of the CH<sub>2</sub> groups, wagging of S-H, or C-C stretching at 873 cm<sup>-1</sup> is also seen. To determine the nature of the species surrounding the platinum nanoparticles, further studies were undertaken by FTIR and elemental analyses. Observation of almost identical spectra for carbon XC-72 and all catalysts without any carbon support is quite interesting. The spectra seem to indicate that structurally these species are similar. Also suggesting that the original surfactants structure, which is responsible for the initial nanoparticle formation, is no longer intact. This is contrary to current thinking in the literature (Eklund, 2004). To investigate this discrepancy, elemental analyses of the catalysts were undertaken and the results are shown in Table 3. 2. As can be seen in this table, C, H, and S elemental analysis of 1-hexanethiol and tert-octanethiol are not consistent with any of the species surrounding the platinum nanoparticles. It is consistently seen that the C/H and C/S ratios are higher than would theoretically be expected for 1-hexanethiol and *tert*-octanethiol. The S/H ratio is always lower than would be expected. The reason for this might be due to decomposition of 1-hexanethiol and *tert*-octanethiol during the reduction and cleaning process. It should be noted, however, that the platinum nanoparticles have not been cleaned completely as sulfur hydrocarbons are present in all the catalysts.



**Figure 3. 6**. FTIR spectra of (a) 1-hexanethiol, (b) *tert*-octanethiol, (c) carbon XC-72, (d) catalyst I, (e) catalyst II, (f) catalyst III, and (g) catalyst IV.

-							
	% C	%Н	% S	%C+%H+%S	% C	% C	% S
					% H	% S	% H
Catalyst I*	14.05	1.05	1.33	16.43	13.4	10.6	1.3
Catalyst II*	12.64	1.20	1.71	15.55	10.5	7.4	1.4
Catalyst III*	15.11	0.97	0.87	16.95	15.6	17.4	0.9
Catalyst IV*	10.37	1.68	1.45	13.50	6.2	7.2	0.9
1-hexanethiol <sup>†</sup>	61.02	11.86	27.12		5.1	2.3	2.3
Tert-octanethiol <sup>†</sup>	64.86	13.52	21.62		5.0	3.0	1.7

Table 3. 2. Experimental and calculated C, H and S elemental analyses results.

\* Experimental and <sup>†</sup> Calculated results.

# 3.1.3. X-RAY PHOTOELECTRON SPECTROSCOPY (XPS) OF CATALYSTS I, II, III AND IV

X-ray photoelectron spectroscopy (XPS) was used to investigate the oxidation state of platinum and sulfur for the prepared catalysts. For this purpose, the Pt 4f and S 2p regions of spectrum were analyzed. Gaussian-Lorentzian method was used for fitting of all XPS peaks and the background was subtracted by means of Shirley's method and all peaks were analyzed in terms of relative peak area and chemical shifts of Pt and S.

For all XPS spectrum, C1s peak (284.6 eV) was taken as a reference and the charging effects were corrected according to that value. As it was shown in Figure 3. 7, the Pt 4f signal consists of two pairs of doublet which had almost equal half-widths with an intensity ratio of ca. 3:4 and the spin orbit splitting of 3.33 eV. XPS analysis of Catalysts I, II, III and IV are also summarized in Table 3. 3 and the Pt 4f electron spectra of all catalysts are a good fit using two doublets with Pt4f<sub>7/2</sub> binding energies of 71.0-71.5 eV and 74.3-74.5 eV. The line at 71.0 – 71.7 eV is

undoubtedly due to Pt(0), whilst the higher binding energy component, 74.3-74.5 eV, is most probably due to the presence of Pt(IV) species such as PtO<sub>2</sub> or Pt(OH)<sub>4</sub>. Previously, it has been shown that for Pt(OH)<sub>4</sub>, the Pt4f<sub>7/2</sub>  $E_b$  was at 74.4 eV (Goodenough, 1988), and for PtO<sub>2</sub>, it was between 74.6 and 74.9 eV (Watanabe, 1987). In addition to identifying the surface species, XPS enables quantification of the various oxidation states of a particular element present. The Pt(0)/Pt(IV) ratio is approximately 7/3 for Catalysts I and III, which has the maximum methanol oxidation reaction current at lower potentials, will be given in section 3. 4, and 8/2 and 6.5 /3.5 for Catalysts II and IV. It is not clear what should be the optimum Pt(0)/Pt(IV) ratio in catalyzing the methanol oxidation reaction, because XPS is an ex-situ technique, consequently, it is difficult to predict the Pt(0)/Pt(IV) ratio on the surface of catalyst during the methanol oxidation reaction. However, considering these data, it might be predicted that a 7/3 ratio of Pt (0) to Pt (IV) gives the best catalytic activity.





Figure 3. 7. Pt 4f electron spectra of catalyst I (a), II (b), III (c) and IV (d).





Figure 3. 7.(contd) Pt 4f electron spectra of catalyst I (a), II (b), III (c) and IV (d).

**Table 3. 3.** Pt  $4f_{7/2}$  core binding energies, eV, in the Catalyst I, II, III and IV. The number in parentheses are the relative intensities of the species.

Samples	Metal	Metal –oxide	
	4f <sub>7/2</sub>	4f <sub>7/2</sub>	
Catalyst I	71.2 (71)	74.4 (29)	
Catalyst II	71.3 (83)	74.3 (17)	
Catalyst III	71.0 (76)	74.4 (24)	
Catalyst IV	71.5 (65)	74.5 (35)	

The sulfur 2p region of XPS was evaluated for each catalyst. All spectra could be fitted using a 2:1 peak area ratio and a 1.2 eV splitting, as shown for Catalyst I in Figure 3. The S 2p spectrum has two doublets due to the presence of two kinds of sulfur. The first doublet with a binding energy of the S  $2p_{3/2}$  peak is 162.8 eV, is consistent with a sulfur atom bound to the platinum surface as a thiolate species. This is in agreement with the previous literature results reported for thiols bound on a Au surface (Castner, 1996). The second doublet with a binding energy of S  $2p_{3/2}$  is 164.2 eV, and is due to unbound thiol, or disulfide within or on top of the thiolate adlayer as reported by Zubraegel et al. (Zubraegel, 1995) These results also shows the presence of sulfur on the surface of the platinum nanoparticles which is consistent with the elemental analysis data.



Figure 3. 8. S 2p electron spectra of catalyst I.

# 3.1. 4. CYCLIC VOLTAMMETRIES (CVs) OF CATALYSTS I, II, III AND IV

Cyclic voltammograms of catalysts I-IV in 0.1 M HClO<sub>4</sub> at room temperature were recorded several times over a 3 month period, and no change was observed, indicating the stability of the prepared catalysts. All cyclic voltammograms were similar in pattern, and an example is shown in Figure 3. 9. Typical hydrogen and oxygen adsorption and desorption features were observed on the platinum nanoparticles. The addition of methanol to the electrolyte resulted in a dramatic change in the appearance of the voltammograms due to the methanol oxidation reaction taking place on the surface of platinum nanoparticles (Figure 3. 10)

Only the anodic part of the cyclic voltammograms for Catalyst I, II, III and IV are shown in Figure 3. in order to compare the activity of catalysts towards the methanol oxidation reaction. The maximum current for methanol oxidation reaction for forward scan was observed at about 0.62 V, 0.66 V, 0.65 V and 0.78 V for Catalyst I, Catalyst II, Catalyst III and Catalyst IV, respectively. The peak positions for Catalyst I and III were observed at lower potentials than Catalysts II and IV. However, the activity of Catalysts III and IV (250 mA/mg Pt) at maximum current potential values was about 1.7 times higher than Catalysts I and II (150 mA/mg Pt). It is also possible to compare the peak position of the catalysts within each group. The peak position of catalysts I and III was observed at a lower potential than catalysts II and IV. These results might be explained by C, H and S content in the catalyst. For instance, when analyzing elemental composition data, it is noted that the sum of the C, H, and S contents for catalyst I (16.43 %) and catalyst III (16.95 %) were higher than catalyst II (15.55 %) and catalyst IV (13.50 %). It is also noticed that although the sum of the C, H, and S percentages for catalysts I and III are higher, the sulfur content of catalysts I (1.33 %) and III (0.83 %) was lower than catalysts II (1.71 %) and IV (1.45 %). So in terms of percent sulfur, catalysts II and IV have measurable more sulfur. We believe the sulfur, which probably is chemisorbed or adsorbed on the surface of platinum nanoparticles (as shown by XPS data), retards the methanol oxidation reaction at high potentials.



Figure 3. 9. Cyclic voltammogram of catalyst I in 0.1 M HClO<sub>4</sub> at room temperature. Scan rate is 50 mV/s.



Figure 3. 10. Cyclic voltammogram of catalyst I in 0.1 M HClO<sub>4</sub> and MeOH at room temperature. Scan rate is 50 mV/s.



**Figure 3. 11.** Anodic part of the cyclic voltammogram of catalysts in 0.1 M HClO<sub>4</sub> + 0.5 M CH<sub>3</sub>OH at room temperature. Scan rate is 50 mV/s.

Comparison of maximum current values for the methanol oxidation reaction with literature values also shows quite interesting results. For example, maximum current values for Pt/MWNT (multiwall carbon nanotubes) and a commercial catalyst E-TEK 40% Pt/Vulcan XC-72 are seen at ~140 mA/g Pt and ~75 mA/g Pt, respectively, which indicates that our catalysts, are ~3.3 and ~1.8 times respectively more active than the commercial catalyst and Pt/MWNT (Kim, 2006).

The performance of a catalyst can also be defined by the ratio of  $I_f/I_b$  where  $I_f$  is the current in the forward scan and  $I_b$  is the current in the reverse scan. High  $I_f/I_b$  ratio indicates good methanol oxidation to carbon dioxide during anodic scan and low accumulation of carbonaceous residues on the surface of catalyst. Low  $I_f/I_b$  ratio shows the opposite. This ratio was found to be ~0.87 for heat treated Pt/C catalyst by Liu and et al. (Liu, 2006) and, between 0.96 and 1.4 for various Pt/Ru catalysts by T.

C. Deivaraj and J. Y. Lee (Deivaraj, 2005) The  $I_f/I_b$  ratio was determined to be 9.44, 5.40, 3.80 and 1.25 for Catalyst I, II, III and IV, respectively. Such a high value for Catalyst I and II indicate that large amount of intermediate carbonaceous species, mostly in the form of linearly bonded Pt=C=O, was oxidized to carbon dioxide in the forward scan as shown below equation (Liu, 2004). In other words, poisoning of catalyst during methanol oxidation is quite small for our catalysts compared to the other catalysts reported in the literature.

$$Pt(OH)_{ads} + Pt=C=O \rightarrow CO_2 + 2Pt + H^+ + e-$$

Generally, elemental analyses and FTIR and X-ray photoelectron spectroscopy results do not show an appreciable difference between the Catalyst I, II and III, IV catalysts. X-ray diffraction and transmission electron microscopy, however, show a difference in particle size of  $2 \pm 0.4$  nm for Catalysts I and II and  $3 \pm 0.4$  nm for Catalysts III and IV. Therefore, it is hypothesized that the particle size parameter might be a dominant factor in the activity of catalysts which we prepared. It is wellknown from mechanistic studies of the methanol oxidation reaction that there is adsorption of methanol and water molecules on the surface of platinum to form HCO<sub>ads</sub> (or COH<sub>ads</sub>) and H<sub>2</sub>O<sub>ads</sub> (or OH<sub>ads</sub>), and then oxidation of those adsorbed species to produce carbon dioxide. To get adsorption of those species on the surface of the platinum, a sufficient surface area is needed. Consequently, it is thought that the optimum size for platinum nanoparticles to catalyze the methanol oxidation reaction is about 3 nm, which was the size observed for Catalysts III and IV.

#### **3.1. 5. CONCLUSIONS FOR CATALYSTS I, II, III AND IV**

Carbon supported platinum nanoparticle catalysts have been prepared using different starting metal complexes, PtCl<sub>4</sub> and H<sub>2</sub>PtCl<sub>6</sub>, and surfactants, 1-hexanethiol and tert-octanethiol, the latter has been used for the first time in this type of synthesis. It has

been found that the structure of surfactant has an effect on the final size of metal nanoparticles, for example the branched structure of tert-octanethiol causes an increase in the size of metal nanoparticles. The optimum platinum nanoparticle size and Pt(0) to Pt(IV) ratio towards methanol oxidation reaction among the prepared catalysts was found to be about 3 nm and 7/3, respectively, which yield quite active catalysts compared to the others. It has been noted that a decrease in the sulfur content of sulfur hydrocarbon causes initialization of the methanol oxidation reaction at lower potentials, presumably due to an increase in the active surface area of platinum nanoparticles. It has been also found that 1-hexanethiol and *tert*-octanethiol decompose during the preparation steps to form sulfur hydrocarbons and those species could not be completely removed from all of the catalysts.

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3. 2. CHARACTERIZATION AND ELECTROCHEMICAL STUDIES FOR CATALYST I (PtCl<sub>4</sub>+1-hexanethiol, as prepared), CATALYST Ia (PtCl<sub>4</sub>+1hexanethiol, 200 °C, 4 h), CATALYST Ib (PtCl<sub>4</sub>+1-hexanethiol, 300 °C, 4 h), CATALYST Ic (PtCl<sub>4</sub>+1-hexanethiol, 400 °C, 4 h), CATALYST II (H<sub>2</sub>PtCl<sub>6</sub>+1hexanethiol, as prepared), CATALYST IIa (H<sub>2</sub>PtCl<sub>6</sub>+1-hexanethiol, 200 °C, 4 h), CATALYST IIb (H<sub>2</sub>PtCl<sub>6</sub>+1-hexanethiol, 300 °C, 4 h), CATALYST IIc (H<sub>2</sub>PtCl<sub>6</sub>+1-hexanethiol, 400 °C, 4 h)

#### 3.2. 1. XRD and TEM OF CATALYSTS I, IA, IB, IC, II, IIA, IIB AND IIC

The powder XRD patterns of Catalysts I, Ia, Ib, Ic, II, IIa, IIb and IIc are shown in Figure 3. 12 and Figure 3. 13. All these catalysts exhibit the characteristic diffraction peaks for face-centered cubic crystal structure of platinum and the bandwidths become sharper and more intense in the manner of increase in temperature during heat treatment step. The average particles size of the crystallite metal species was calculated from X-ray powder diffraction data by Scherrer formula (Klug, 1962) as given in Chapter 3. 1. Using this formula, calculated average particle sizes of the platinum were found to be ~2.00, ~2.56, ~4.23, ~4.52, ~2.13, ~2.77, ~4.29 and ~4.62 for Catalysts I, Ia, Ib, Ic, II, IIa, IIb and IIc, respectively, Table 3. 4.



Figure 3. 12. X-ray diffractograms of Catalyst I, Ia, Ib and Ic.



Figure 3. 13. X-ray diffractograms of Catalyst II, IIa, IIb and IIc.

Samples	a (particle size in nm)	b (particle size in nm)
Catalyst I (no heating)	~2.00	~1.8 - 2.2
Catalyst Ia (200°C, 4h heating)	~2.56	~1.1 - 4.0
Catalyst Ib (300°C, 4h heating)	~4.23	~1.3 - 4.5
Catalyst Ic (400°C, 4h heating)	~4.52	~1.5 - 5.0
Catalyst II (no heating)	~2.13	~2.3 - 2.7
Catalyst IIa (200°C, 4h heating)	~2.77	~2.7 - 5.0
Catalyst IIb (300°C, 4h heating)	~4.29	~3.5 - 5.5
Catalyst IIc (400°C, 4h heating)	~4.62	~3.7 - 6.0

**Table 3. 4.** Average crystallite platinum particles size determined by a) X-ray line broadening and b) transmission electron microscopy.

To observe individual nanoparticles, TEM was employed. In all catalysts, relatively narrow range of platinum particle size was obtained and an example is shown for Catalyst IIa in Figure 3. 14. Examination of individual platinum nanoparticles indicated that particle size of platinum changes between 1.8 - 2.2 nm, 1.1 - 4.0 nm, 1.3 - 4.5 nm, 1.5 - 5.0 nm, 2.3 - 2.7 nm, 2.7 - 5.0 nm, 3.5 - 5.5 nm and 3.7 - 6.0 nm for Catalysts I, Ia, Ib, Ic, II, IIa, IIb and IIc, respectively and these results are in agreement with XRD data. As expected, thermal treatment induces a growth of platinum nanoparticles, (Kawaguchi, 2005; Yang, 2005) however the agglomeration of particles are limited presumably due to formation of a sulfur hydrocarbon protective layer around platinum nanoparticles (Kuo, 2006). This theory reinforced by our FTIR data.





Figure 3. 14. Transmission electron micrograph and histogram of the particle size distribution of Catalyst IIa.

# 3.2. 2. FTIR OF CATALYSTS I, IA, IB, IC, II, IIA, IIB AND IIC

The FTIR spectra of carbon XC-72, 1-hexanethiol, and all the catalysts without carbon support are shown in Figure 3. 15. The FTIR spectrum of 1-hexanethiol is different from the spectra of all the catalysts. It has quite strong characteristic bands between 2000 and 400 cm<sup>-1</sup>. On the other hand, the FTIR spectra of carbon XC-72 and all the catalysts without any carbon support are almost identical, indicating that these species are structurally similar. The bands between 1350 and 1550 cm<sup>-1</sup> are attributed to scissoring of CH<sub>2</sub> groups, and the sharp band at 873 cm<sup>-1</sup> has been assigned to rocking of the CH<sub>2</sub> groups, wagging of S-H, or stretching of C-C (Sen, 2007). In other words, this result most probably indicates the decomposition of 1hexanethiol during reduction and/or the cleaning process to form sulfur hydrocarbon compound(s), which is uncharacterized apart from elemental analysis, for all the catalysts. To do this, C, H, and S elemental analyses of catalysts Ia and IIa before carbon support addition were obtained by inductively coupled plasma spectroscopy, and the results are given in Table 3. 5. As can be seen from the table, theoretical C, H, and S elemental analyses for hexanethiol are totally different from catalysts Ia and IIa, which is to be expected, because the catalysts contain platinum nanoparticles. The comparison of data can only be done by considering the ratios of C/H, C/S, and S/H, which are also given in Table 3. 5. It is consistently observed that the C/H and C/S ratios are higher than that theoretically expected for 1-hexanethiol, while the S/H ratio is always lower than that expected. The existence of large amounts of carbon and small amounts of hydrogen and sulfur in all the catalysts compared to the theoretical data for 1-hexanethiol, and the differences in FTIR spectra suggest that 1hexanethiol has decomposed to form some kind of sulfur hydrocarbon. In other words, this result shows that the platinum nanoparticles have not been cleaned completely by the washing process and that sulfur hydrocarbon compounds are present in all the catalysts. The amount of structurally unknown sulfur hydrocarbon (or impurity in the catalysts) is not negligible; its percentage varies between about 15 and 16 %, Table 3. 5.



**Figure 3. 15.** FTIR spectra of (1) 1-hexanethiol, (2) Carbon XC-72, (3) catalyst I, (4) catalyst Ia, (5) catalyst Ib, (6) catalyst Ic, (7) catalyst II, (8) catalyst IIa, (9) catalyst IIb, and (10) catalyst IIc.

	% C	% H	% S	%C+%H+%S	% C	% C	% S
					% H	% S	% H
Catalyst Ia*	14.05	1.05	1.33	16.43	13.4	10.6	1.3
Catalyst IIa*	12.64	1.20	1.71	15.55	10.5	7.4	1.4
1-hexanethiol <sup>†</sup>	61.02	11.86	27.12	100	5.1	2.3	2.3

Table 3. 5. Experimental and calculated C, H and S elemental analyses results.

\* Experimental and <sup>†</sup> Calculated results.

#### **3.2. 3. CVs OF CATALYSTS I, IA, IB, IC, II, IIA, IIB AND IIC**

The cyclic voltammograms of all the catalysts in 0.1 M HClO<sub>4</sub> at room temperature were recorded several times within 2 months, and no change was observed, indicating the stability of the prepared catalysts. Similar patterns were obtained from each one and one example is shown in Figure 3. 16. A typical hydrogen and oxygen adsorption and desorption peaks were observed clearly. An addition of methanol to the HClO<sub>4</sub> electrolyte causes a dramatic change in the pattern of the voltammograms, which exhibits a classical methanol oxidation response, Figure 3. 17. The methanol oxidation reaction on carbon supported platinum catalyst electrodes is characterized on the anodic sweep where a weak hydrogen desorption region followed by a double layer region before the onset of methanol oxidation near 0.2 V. Above 0.65 V, methanol oxidation is inhibited due to formation of an inactive OH<sub>ads</sub> (Biegler, 1973) or platinum oxide layer (Hampson, 1979) and the anodic current decreases until the potential is swept into oxygen evolution region. On the reverse scan, a weak feature corresponding to platinum oxide reduction is often observed before methanol oxidation recommences around 0.5 V.



**Figure 3. 16.** Cyclic voltammogram of Catalyst Ia in 0.1 M  $HClO_4$  at room temperature. Scan rate is 50 mV/s.



**Figure 3. 17.** Cyclic voltammogram of Catalyst IIa in 0.1 M HClO<sub>4</sub> and 0.5 M CH<sub>3</sub>OH at room temperature. Scan rate is 50 mV/s.

In order to represent the methanol oxidation reaction clearly, the anodic part of the cyclic voltammograms for all the catalysts are shown in Figure 3. 18 and 3. 19. As can be seen in those figures, the current density of electro-oxidation of methanol decreases regularly with the increase in the heat treatment temperature of catalysts. The performance of Catalyst IId, which was heated up at 400°C for 4 hours, towards methanol oxidation reaction is one-third that of Catalyst Ia. On the other hand, for Catalyst I, a sudden decrease in the activity of Catalysts Ic and Id was observed compared to Catalysts Ia and Ib. Again, the catalytic activity of Catalysts Ic and Id decreases by one-third compared to Catalysts Ia and Ib and same is observed for Catalyst II. There are two possibilities to explain these data. The first reason is that as the temperature increases during the heating process, it causes an increase in the particle size of platinum nanoparticles as observed in our experimental results, which would then decrease the active surface area of the catalysts (Babu 2005; Liu, 2004). However, Z. Liu and co-workers observed just opposite result. They found out that the heat treated catalysts were more active than the non-heat-treated ones, because of removal of the organic surfactant shell (Sen, 2007). So, the second postulate which might explain our results is based on an alteration of the binding energies of Pt  $4f_{7/2}$ region, which was determined by XPS.



**Figure 3. 18.** Anodic part of the cyclic voltammogram of catalysts in  $0.1 \text{ M HClO}_4 + 0.5 \text{ M CH}_3\text{OH}$  at room temperature. Scan rate is 50 mV/s.



**Figure 3. 19.** Anodic part of the cyclic voltammogram of catalysts in 0.1 M HClO<sub>4</sub> + 0.5 M CH<sub>3</sub>OH at room temperature. Scan rate is 50 mV/s.

# 3.2. 4. XPS OF CATALYSTS I, IA, IB, IC, II, IIA, IIB AND IIC

X-ray photoelectron spectroscopy has been used to obtain information about the oxidation state of platinum nanoparticles and their relative intensities. The platinum 4f electron spectra are shown in Figure 3. 20 and 3. 21. The same fitting parameters given in Chapter 3.1.4 were used for all XPS data. The Pt 4f electron spectra of all the catalysts are well resolved with two doublets with Pt  $4f_{7/2}$  binding energies of between 71.2-72.2 eV and between 74.3-75.5 eV. The line at lower binding energies is undoubtedly due to Pt (0), whilst the higher binding energy component is due to a Pt(IV) species such as PtO<sub>2</sub> or Pt(OH)<sub>4</sub> (Tian, 2006). Although, it has been previously shown that the binding energy of Pt  $4f_{7/2}$  for Pt(OH)<sub>4</sub> is 74.4 eV (Goodenough, 1988) and for PtO<sub>2</sub>, it is 74.6-74.9 eV (Watanabe, 1987), it is quite difficult to determine what oxygen containing groups, O<sup>2-</sup>, OH<sup>-</sup> or H<sub>2</sub>O, are bonded to the platinum. In principle, this could be achieved by considering the relative intensities of the platinum 4f and oxygen 1s peaks, however, the majority of the oxygen containing groups identified in the XPS are affected by the attached oxygens to the carbon support. Therefore, it is difficult to differentiate whether the attached oxygen is coming from carbon or platinum.

The relative intensities of the platinum species (Pt (0) and Pt (IV)) are given in Table 3. 6. The results reveal that the metallic Pt(0) is the major species in all the catalysts (> 70 %) with small amount of an oxidized platinum species (< 30 %). It is believed that catalyst with Pt (0) oxidation state provides active site for methanol oxidation reaction rather than the Pt (IV) species (Kuo, 2006). Therefore, having large amount of metallic Pt (0) for these platinum-based catalyst is required for high catalytic activity. However, some of the observed Pt  $4f_{7/2}$  binding energies for Pt (0) are noticeably higher (71.2-72.2 eV) than that of either bulk platinum ( $4f_{7/2} = 71.2 \text{ eV}$ ) (Allen, 1974; Kim, 1971) or platinized carbon electrodes ( $4f_{7/2} = 71.2 \text{ eV}$ ) (Kuo, 2006; Syzmanski, 1984; Goodenough, 1987). The positive shift in binding energy corresponds to a decrease in the electronic charge density on the platinum atoms present in the prepared catalysts (Gokagac, 2002). This might arise from metal-

support interactions where there might be an electron shift from metal to carbon support. The Pt  $4f_{7/2}$  binding energy value increases going from Catalysts I to Ia to Ib to Ic. Similar trends were observed for Catalysts II, IIa, IIb and IIc.



Figure 3. 20. Pt 4f electron spectra of catalyst I (a), Ia (b), Ib (c) and Ic (d).



Figure 3. 20.(contd) Pt 4f electron spectra of catalyst I (a), Ia (b), Ib (c) and Ic (d).



Figure 3. 20.(contd) Pt 4f electron spectra of catalyst I (a), Ia (b), Ib (c) and Ic (d).



Figure 3. 21. Pt 4f electron spectra of catalyst II (a), IIa (b), IIb (c) and IIc (d).

d)



Figure 3. 21. (contd) Pt 4f electron spectra of catalyst II (a), IIa (b), IIb (c) and IIc (d).



Figure 3. 21.(contd) Pt 4f electron spectra of catalyst II(a), IIa(b), IIb(c) and IIc(d).

Samples	Metal	Metal –oxide
	4f <sub>7/2</sub>	4f <sub>7/2</sub>
Catalyst I (no heating)	71.2 (72)	74.4 (28)
Catalyst Ia (200°C, 4h heating)	71.7 (70)	75.0 (30)
Catalyst Ib (300°C, 4h heating)	72.0 (73)	75.2 (27)
Catalyst Ic (400°C, 4h heating)	72.1 (74)	75.4 (26)

71.3 (83)

71.8 (80)

72.0 (68)

72.2 (72)

74.3 (17)

75.2 (20)

75.3 (32)

75.5 (28)

**Table 3. 6.** Pt  $4f_{7/2}$  Core Binding Energies, eV, in catalysts I, Ia, Ib, Ic, II, IIa, IIb, IIc<sup>a</sup>

<sup>a</sup> The numbers in parentheses are the relative intensities of the species.

**Catalyst II (no heating)** 

Catalyst IIa (200°C, 4h heating)

Catalyst IIb (300°C, 4h heating)

Catalyst IIc (400°C, 4h heating)

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The known mechanism, which was explained by in-situ and ex-situ spectroscopic techniques, for methanol oxidation reaction on the platinum surface is composed of the following steps (Hampson, 1979; Szymanski, 1984; Gasteiger, 1993, Ticarelli, 1989; Gasteiger, 1994; Anderson, 1995; Hamnett, 1997):

a) The consumption of three electrons during formation and oxidation of the adsorbate:

 $CH_3OH \rightarrow HCO_{ads} + 3H^+ + 3e^-$  or  $CH_3OH \rightarrow COH_{ads} + 3H^+ + 3e^-$ 

b) Adsorption of H<sub>2</sub>O molecules:

 $H_2O \rightarrow H_2O_{ads} \qquad \qquad \text{or} \qquad OH \rightarrow OH_{ads}$ 

c) Oxidation of the adsorbates:

 $\text{COH}_{\text{ads}} \text{ (or HCO}_{\text{ads}}) + \text{H}_2\text{O}_{\text{ads}} \text{ (or OH}_{\text{ads}}) \rightarrow \text{CO}_2 + 3\text{H}^+ + 3\text{e}^-$ 

It is believed that the deficiency of electronic charge density on the Pt (0) might cause a decrease in the number of adsorption of organic molecules, which are adsorbed on the surface of platinum, which are required for methanol oxidation reaction. So this is a possible reason for the decrease in the activity of catalysts when moving along the series I to Ia to Ib to Ic where the Pt 4f7/2 binding energy value shifts from 71.2 (I) to 71.7 (Ia) to 72.0 (Ib) to 72.1 eV (Ic), and this is also seen in catalysts II, IIa, IIb and IIc (Table 3. 6), as it mirrors the trend seen in the electronic charge density on Pt (0); i.e., it decreases along the series catalysts I, Ia, Ib, Ic and catalysts II, IIa, IIb and IIc.

# 3.2. 5. CONCLUSIONS FOR CATALYSTS I, IA, IB, IC, II, IIA, IIB AND IIC

The syntheses of different size of platinum nanoparticles supported on Carbon XC-72 have been achieved through the reduction of  $PtCl_4$  and  $H_2PtCl_6$  by superhydride using 1-hexanethiol as a surfactant. The crystal structure of platinum for all the catalysts was determined by XRD and found to be face-centered cubic. The average size of platinum nanoparticles was calculated from X-ray diffraction peak widths using the Schreer formula and individual platinum nanoparticle size was determined by transmission electron microscopy. The results are in agreement with each other. The average size of the platinum nanoparticles increases with increase in the heat treatment temperature, however, there is no formation of large agglomerated particles for any of the catalyst. The oxidation state of platinum and their relative intensities were determined by XPS. It was found that a significant amount of platinum was in zero oxidation state (> 70 %) and Pt  $4f_{7/2}$  binding energy values positively shifted as temperature increased (going along the series Catalysts I, Ia, Ib, Ic and II, IIa, IIb and IIc. This positive shift might be due to electron transfer from platinum nanoparticles to carbon support during the heat treatment step. It is believed that the decrease in the electronic charge density on Pt (0) might cause a decline in the number of organic molecules adsorbed, which are needed for methanol oxidation reaction; this then causes a decrease in the performance of catalyst in the methanol oxidation reaction. Consequently, the activity of catalyst decreases as the temperature increases (Catalysts I > Ia > Ib > Ic and the same trend was observed for Catalysts II).

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3. 3. CHARACTERIZATION AND ELECTROCHEMICAL STUDIES FOR CATALYST A (70 % Pt + 30 % Ru + tert-octanethiol), CATALYST B (80 % Pt + 20 % Ru + tert-octanethiol), CATALYST C (90 % Pt + 10 % Ru + tertoctanethiol)

#### 3.3.1. XRD AND TEM OF CATALYSTS A, B AND C

X-ray diffraction was used to reveal information on the bulk structure of the prepared catalysts. PtRu catalysts also exhibited the characteristic diffraction peaks for the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of face centered cubic structure of platinum and the peak positions of (1 1 1) and (2 2 0) are given in Table 3. 7. It is clearly seen from the XRD data that the diffraction peak positions in the PtRu/C catalysts are slightly shifted to higher 20 values in the order of Pt/C, catalysts B, C and A. The lattice parameter (a) of the prepared samples were calculated from the reflections of (1 1 1) and (2 2 0) and are provided in Table 3. 7. The lattice parameters change from 3.925 Å, 3.921 Å, 3.910 Å, 3.861 Å for Pt/C, catalysts B, C and A, respectively. The reduction of lattice parameter in the prepared PtRu/C catalysts arises primarily from the substitution of platinum atoms by ruthenium atoms, which causes the contraction of the fcc Pt crystalline lattice, indicating the formation of PtRu alloys. According to Vegard's law, the lattice parameter can be used to determine the extent of alloying and atomic fraction of ruthenium,  $\chi_{Ru}$ , in the PtRu/C catalysts and those parameters were calculated using equation 1 (Antolini, 2000; Chu, 1996; Liu, 2004); the results are given in Table 3. 7. and also shown in Figure 3. 22.

$$a_{fcc} = l_{oc} - k\chi_{Ru} \tag{1}$$

where  $a_{fcc}$  = the lattice parameter for the PtRu/C catalyst,  $l_{oc}$  = the lattice parameter for pure carbon supported platinum, 3.925 Å, and k = the lattice constant, 0.124 Å. It is known that it is difficult to evaluate the degree of alloying for a supported alloy, because the lattice parameter of pure supported platinum is lower than that of unsupported platinum due to platinum-carbon interaction. Here it is assumed that the dependence of lattice constant on ruthenium content is the same for both unsupported and supported alloys. The atomic percentages of platinum and ruthenium were calculated by utilizing the above formula and the elemental analyses of platinum and ruthenium in the prepared catalysts (Table 3. 7). The results of the atomic percentage of platinum and ruthenium are different in the elemental analysis and XRD data. This is most probably due to the difference between the two techniques. As it is known very well, the elemental analysis results give atomic percentage of crystalline or noncrystalline platinum and ruthenium elements while XRD results give only the crystalline form of platinum and ruthenium metal and/or compound.

In addition to this the atomic percentage of ruthenium which was not incorporated into PtRu alloy was computed by comparing elemental analyses and XRD results, Table 3. 7. Calculations show that Ru is present in 92.0, 8.7 and 53.3 percentages in the platinum crystal to form PtRu alloy for catalysts A, B and C, respectively. In other words, most of the ruthenium in catalyst B (> 90 %) and almost half of the ruthenium (~ 47 %) in catalyst C exist as a crystalline and/or amorphous Ru and  $RuO_2$ . On the other hand, almost all of the ruthenium (> 90 %) was incorporated into fcc Pt crystalline structure to form a PtRu alloy in catalyst A. There is no evidence for the formation of hexagonal close-packed ruthenium and/or rutile RuO<sub>2</sub> crystallites in any of the prepared catalysts. However, it does not mean there is no formation of those species, because it has also been reported that the PtRu alloys containing up to 52 wt % of Ru would show only Pt reflections from the platinum face-centered cubic structure (Chu, 1996). In addition to this, it should be stressed that it is always possible that there could be some metallic Ru and its oxides in the amorphous state (Guo, 2005). Moreover, the other point that should be emphasized here is that as the ruthenium insertion to the platinum crystallite increases, the difference between the elemental and the XRD results get smaller. For example, the atomic percentage difference is 4.53, 10.46, and 29.68 for catalysts A, C, and B where percentage insertion of Ru to Pt is 92, 53.3, and 8.7 %, Table 3.7.
**Table 3. 7.** The peak positions of  $(1\ 1\ 1)$  and  $(2\ 0\ 0)$  in 2 $\theta$ , lattice parameter (a in A°), atomic percent of platinum and ruthenium calculated form Pt and Ru elemental analyses and X-ray data, and ruthenium percent which incorporated in PtRu alloy in catalysts A, B and C.

Samples	(h,k,l) (1 1 1)	(h,k,l) (2 0 0)	а	Atomic % of Pt*	Atomic % of Ru*	Atomic % of Pt**	Atomic % of Ru**	Incorporated Ru %
Pt/C	39.50	67.90	3.925					
Catalyst C	39.65	68.20	3.910	77.6	22.4	88.06	11.94	53.3
Catalyst B	39.52	68.00	3.921	67.5	32.5	97.18	2.82	8.7
Catalyst A	39.90	69.75	3.861	43.7	56.3	48.23	51.77	92.0

Atomic percent calculated from Pt and Ru elemental analyses\* and X-ray diffraction data\*\*.



**Figure 3. 22.** Dependence of f.c.c. lattice constant (a in Å) on the Ru content of the prepared catalysts.

The size and distribution of the metal particles on the carbon support has been determined by TEM. Transmission electron micrographs of the carbon supported platinum powder sample show that platinum nanoparticles ( $PtCl_4 + tert$ -octanethiol, catalyst I) appear to be uniformly distributed on the carbon support and there is no evidence for agglomeration of the platinum crystallites. The size of the platinum nanoparticles is about  $3 \pm 0.4$  nm. The particles observed in TEM studies of the catalysts A, B and C powders show an entirely different pattern to that which is seen in the previously reported Pt/C powder sample. In general, the majority of metal particles in catalysts B and C are in the range of 0.5-3 nm diameter, and are uniformly dispersed on the carbon support. In addition to these particles, considerable amounts of somewhat larger clusters ca. 4-40 nm diameter, which appear to consists of a number of particles, are also evident, this is shown in Figure 3. 23 (catalyst B). In addition to these two types of small particles, which comprise the vast majority of these samples, on relatively rare occasions extremely large crystallite particles, around 200-300 nm diameter, were observed. These large crystallites are most probably due to combination of the small individual particles during the catalysts formation. Catalyst A shows completely different type of metal particle distribution on the carbon support. The electron micrographs of this catalyst indicate that most of the particles are between 100-300 nm diameters and it was difficult to observe small metal particles. This might be due to the different surfactant to metal precursors (RuCl<sub>3</sub> + PtCl<sub>4</sub>) ratio. As can be seen in the Experimental Section, the surfactant to RuCl<sub>3</sub> ratio is 1:1 for all catalysts; however, catalyst A contains the largest amount of RuCl<sub>3</sub> as well as the surfactant. It is wellknown, for the platinum nanoparticle samples, that as the surfactant to metal precursor ratio increases, the size of the micelles gets smaller. Consequently, small platinum nanoparticles are formed. However, in this work, instead of platinum complexes (such as H<sub>2</sub>PtCl<sub>6</sub> and PtCl<sub>4</sub>) RuCl<sub>3</sub> has been added first in the reaction medium. Although the type of interaction between the surfactant and RuCl<sub>3</sub> is not known very well, we believe that the interaction between the surfactant and RuCl<sub>3</sub> is different than the one between the surfactant and PtCl<sub>4</sub>. This might cause a possibility to obtain a different metal nanoparticle size.





**Figure 3. 23.** High angle annular dark field scanning transmission electron micrograph (HAADF STEM) of catalyst B.

Energy dispersive analyses (EDS) of all catalysts indicated that platinum and ruthenium are always present in the expected atomic ratios. For example, for catalysts A, B and C, the atomic percentages for platinum and ruthenium changes from 45-50:55-50 to 65-70:35-30 to 75-80:25-20, respectively, which are close to the elemental analysis results. As an example, electron micrograph and EDS results of region A for catalyst A are given in Figure 3. 24.



**Figure 3. 24.** Transmission electron micrograph of catalyst A(a) and EDS result for region A (b) (42 and 58 atomic percent of Pt and Ru, respectively).



**Figure 3. 24. (contd)** Transmission electron micrograph of catalyst A(a) and EDS result for region A (b) (42 and 58 atomic percent of Pt and Ru, respectively).

#### 3.3. 2. CVs OF CATALYSTS A, B AND C

In order to characterize the surface of metal nanoparticles on the carbon support and/or the extent of interaction between the ruthenium and platinum, the cyclic voltammograms of Pt/C, Ru/C, catalysts A, B and C were recorded in 0.1 M HClO<sub>4</sub> at room temperature with a scan rate of 50 mV/s. As shown in Figure 3. 25, the voltammogram of a freshly prepared Ru/C (10% Ru) electrode showed two redox features which were ascribed to oxidation of the surface Ru (II) to Ru (III) at about 100 mV and Ru (III) to Ru (IV) at about 600 mV on the anodic sweep. Their reduction features were observed at about -200 and +150 mV, respectively, on cathodic sweep (Goodenough, 1990; Burke, 1979, Iwakure, 1977). On the other hand, the cyclic voltammograms of Pt/C, catalysts B and C indicate similar pattern by showing hydrogen and oxygen features as shown in Figure 3. 26. For catalyst A, however, a change in pattern and a decrease in the current associated with the hydrogen adsorption feature was observed. This most probably indicates that there has been a change in the surface groups by insertion of Ru into fcc Pt crystalline to form PtRu alloy. Ru peaks were not observed for any of the catalysts, which might be due to the concealment of these weak peaks under the strong platinum features.



**Figure 3. 25.** Cyclic voltammogram of carbon unsupported ruthenium nanoparticle catalyst in 0.1 M HClO<sub>4</sub> at room temperature. Scan rate is 50 mV/s.



**Figure 3. 26.** Cyclic voltammograms of Pt/C, catalysts A, B and C in 0.1 M HClO<sub>4</sub> at room temperature. Scan rate is 50 mV/s.

Addition of methanol to the HClO<sub>4</sub> electrolyte resulted in a change in appearance of the voltammogram and the typical methanol oxidation reaction was observed for all catalyst, as shown in Figure 3. 27. In order to prevent confusion in the figures, only the anodic part of the cyclic voltammograms is given in Figure 3. 28. As is clearly seen in this figure, the maximum activity (450 mA/ mg Pt at 0.6 V) and lower onset potential (~0.25 V) for the methanol oxidation reaction were observed for catalyst A compared to the other prepared catalysts. As discussed in the XRD section, catalyst A consists of more than 90 % of PtRu alloy where platinum and ruthenium metals are close enough to achieve an easy oxidation of PtCO<sub>ads</sub> and Ru(OH)<sub>ads</sub> to CO<sub>2</sub>. It is believed that this could be one of the important reasons why the methanol oxidation reaction takes place at low potentials and high current density at high potentials. The least active catalyst was catalyst B in which quite small amount of (< 9 %) PtRu alloy formation was observed and most of the Ru does not integrate into fcc Pt crystallites. It is thought that this type of structure, where Pt and Ru are not sufficiently close to each other, possibly does not facilitate the oxidation of methanol to carbon dioxide. The activity of the Pt/C and catalyst C are comparable, which might be due to presence of small amount of ruthenium in the catalyst C making it compositionally similar to Pt/C.



**Figure 3. 27.** Cyclic voltammogram of catalysts A in 0.1 M HClO<sub>4</sub> + 0.5 M CH<sub>3</sub>OH at room temperature. Scan rate is 50 mV/s.



**Figure 3. 28.** Cyclic voltammogram of catalysts A, B, C and Pt/C in 0.1 M HClO<sub>4</sub> + 0.5 M CH<sub>3</sub>OH at room temperature. Scan rate is 50 mV/s.

We also compared the activity of catalyst A with previously reported catalysts. The maximum activity for the commercial catalyst E-TEK 40 % Pt/Vulcan XC-72 was 75 mA / (mg Pt) and for a Pt/MWNT (multiwall carbon nanotubes) it was 140 mA / (mg Pt) (Kim, 2006). This shows that catalyst A is 6 times more active compared to the commercial catalyst and > 3 times more active than the Pt/MWNT.

#### 3.3. 3. XPS OF CATALYSTS A, B AND C

X-ray photoelectron spectroscopy analysis was performed on all samples in order to investigate the oxidation states of platinum and ruthenium and their relative ratios in the nanoparticles. The Pt 4f region of the XPS spectra of catalysts A, B, C and Pt/C (Catalyst I) are shown in Figure 3. 29. Two doublets of Pt  $4f_{7/2}$  and Pt  $4f_{5/2}$  were observed by Gaussian curve fitting and the data are given in Table 3. 8. The Pt  $4f_{7/2}$  appeared at about 71.1 eV for all samples, indicating metallic Pt<sup>0</sup> (Kennedy, 1990). The higher binding energy component appeared about 74.3 eV and can be assigned to Pt<sup>IV</sup> ind PtO<sub>2</sub> and/or Pt(OH)<sub>4</sub> (Ivakure, 1977). The relative intensities of Pt (0) to Pt (IV) revealed that the predominant species is metallic platinum, Table 3. 8.



Figure 3. 29. Pt 4f electron spectra of Pt/C (a), Catalysts A (b), B (c) and C (d).



Figure 3. 29. (contd) Pt 4f electron spectra of Pt/C(a), Catalysts A(b), B(c) and C(d).



Figure 3. 29. (contd) Pt 4f electron spectra of Pt/C(a), Catalysts A(b), B(c) and C(d).

Table 3. 8. Pt  $4f_{7/2}$  and Ru  $3p_{5/2}$  Core Binding Energies, eV, in Pt/C, catalysts A, B and  $C^a$ 

	Pt (0)	Pt (IV)	Ru (0)	Ru (III and/or IV)	Hydrous Ru(IV)	Ru(VI)
Pt/C	71.0	74.4				
	(76 %)	(24 %)				
Catalyst A	71.0	74.2		462.3		465.6
	(70 %)	(30 %)		(75 %)		(25 %)
Catalyst B	71.1	74.3	461.2		464.5	
	(70 %)	(30 %)	(70 %)		(30 %)	
Catalyst C	71.1	74.1	460.9		464.1	
	(69 %)	(31 %)	(78 %)		(22 %)	

<sup>a</sup> The numbers in parentheses are the relative intensities of the species.

d)

Because of overlap of the Ru 3d signal with the C 1s signal from the carbon support, it is difficult to determine the ruthenium content from the Ru 3d region, therefore the Ru  $3p_{3/2}$  region was analyzed and this part of spectrum is shown in Figure 3. 30. The Ru  $3p_{3/2}$  binding energies and their relative integrated intensities are summarized in Table 3. 8. The Ru  $3p_{3/2}$  region could be deconvoluted into two components with binding energies of about 461.1 and 464.3 eV for catalysts B and C. The peak at 461.1 eV can be assigned as metallic Ru (Liu, 2006; Zhang, 2003), while the peak at about 464.3 eV can be attributed as a Ru (IV) species, such as RuO<sub>2</sub> (Marwan, 2005; Rolison, 1999) and the relative intensities of these two peaks showed that most of the ruthenium exists as metallic ruthenium. Generally, the binding energy for RuO<sub>2</sub> was observed between ~462.3 - 462.6 eV (Marwan, 2005; Rolison, 1999) however, it is believed that presence of hydrated RuO<sub>2</sub>, such as RuO<sub>2</sub>.xH<sub>2</sub>O, causes the line shift to higher binding energies, this might be attributed to the presence of OH functionalities on the ruthenium (Kennedy, 1990). From the integrated intensities of the deconvoluted Ru XPS signals, it is found that Ru<sup>0</sup> was the principle oxidation state on the Ru surface for catalysts B and C. The Ru 3p<sub>3/2</sub> region for catalyst A is also composed of two components with binding energies of 462.3 and 465.6 eV. The higher energy peak, 465.6 eV, could be assigned to the higher oxidation state of Ru<sup>VI</sup> in RuO<sub>3</sub> (Arico, 1996; Zhang, 2003; Liu, 2006). However interpretation of lower energy peak, which is the dominant species in the catalyst A, is not as simple as the higher one, because there are several possibilities for this peak. These are a) Ru (IV) such as RuO<sub>2</sub> (Marwan, 2005; Pollini, 1994) and/or RuO(OH)<sub>2</sub>(H<sub>2</sub>O) (Hamnett, 1990) and/or RuO<sub>x</sub>(OH)<sub>4-2x</sub>, and/or b) Ru (III) (Varughese, 2002) such as Ru(OH)<sub>3</sub> and/or RuOx(OH)3-2x. Although, the suggestion of the formation of RuOx(OH)4-2x and/or  $RuO_x(OH)_{3-2x}$  on the surface of the catalysts might be speculative in our case due to lack of Mössbauer facilities, the work of Hamnett and et al, however, indicates the presence of ruthenium oxyhydroxides in their PtRu methanol oxidation anodes (Hamnett, 1990).



Figure 3. 30. Ru 3p electron spectra of Pt/C (a), catalysts A (b), B (c) and C (d).



Figure 3. 30.(contd) Ru 3p electron spectra of Pt/C(a), catalysts A(b), B(c) and C(d).

Differential electrochemical mass spectrometry (DEMS) studies demonstrated that methanol does not adsorb and/or chemisorb on pure ruthenium at room temperature, consequently, Ru itself is inactive for the methanol oxidation reaction at room temperature. It is also known that catalysts formed from platinum and rutile RuO<sub>2</sub> alone are known to be rather inactive for the methanol oxidation reaction (Arico, 1996). However, it is generally observed that the addition of Ru to Pt to form PtRu catalyst enhances the methanol oxidation reaction and the reaction commences at more negative potentials. This observation might be explained by considering <sup>99</sup>Ru Mössbauer data which was obtained by Hamnett et al. (Hamnett, 1990). They have found that ruthenium in PtRu catalysts can be present as ruthenium oxyhydroxide, such as RuO(OH)<sub>2</sub>(H<sub>2</sub>O), and RuO<sub>2</sub>. Using XPS data, we also believe that catalyst A most probably contains RuO<sub>2</sub> as well as RuO<sub>x</sub>(OH)<sub>4-2x</sub> and/or RuO<sub>x</sub>(OH)<sub>3-2x</sub>, which

enhances the methanol oxidation reaction for catalyst A by the following reaction process.

$$PtCO_{ads} + RuO(OH)_{2(ads)} \rightarrow Pt + RuO + CO_2 + H_2O$$

#### 3.3. 4. CONCLUSIONS FOR CATALYSTS A, B AND C

Carbon supported, different atomic percent, platinum-ruthenium (Pt:Ru = 0.8, 2.1and 3.5) nanoparticles have been prepared using a new surfactant, tert-octanethiol, characterized and their activities toward the methanol oxidation reaction have been determined. XRD data indicates that catalyst A consists of more than 90 % of PtRu alloy, while catalyst B is composed of Pt and Ru metals and their oxides and only small amount of (< 9 %) Ru incorporates into fcc platinum crystalline structure to form the alloy. Only half of the Ru in catalyst C forms the PtRu alloy. TEM results showed that platinum nanoparticles  $(3 \pm 0.4 \text{ nm})$  uniformly distributed on the carbon support and there is no agglomeration for carbon supported Pt catalyst. On the other hand, catalyst A, B and C have quite large agglomerated particles in addition to the small ones. EDS analyses showed that Ru and Pt are present in the expected proportions. XPS analyses results demonstrate that Pt is found in two oxidation states, Pt (0) (~ 70 %) and Pt (IV) (~ 30 %) for all the catalysts. Most of the ruthenium in catalysts B and C is found as a metallic Ru and a small amount of Ru (IV), such as RuO<sub>2</sub>.xH<sub>2</sub>O. In catalyst A, a small amount of ruthenium is found as a Ru (VI), such as RuO<sub>3</sub>, and we assume most of the ruthenium is found as ruthenium (IV) oxide and/or ruthenium (III and/or IV) oxyhydroxide, such as RuO<sub>x</sub>(OH)<sub>3-2x</sub> and/or  $RuO_x(OH)_{4-2x}$ . In addition to PtRu alloy formation, which provides a suitable PtRu surface for the methanol oxidation reaction, the formation of ruthenium oxyhydroxide is probably the other reason why the methanol oxidation reaction starts at more negative potentials and the maximum activity is seen at high potentials with

this catalyst. We believe this is the case because of the ability of the ruthenium oxyhydroxide to remove poisoning  $CO_{ads}$  by oxidizing it to  $CO_2$  (g).

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#### **CHAPTER 4**

#### CONCLUSIONS

Carbon-supported platinum and Pt-Ru nanoparticle catalysts have been prepared, analyzed and employed for methanol oxidation reaction to examine the effect of surfactants, heat treatment and addition of Ru to platinum nanoparticles in different ratios. The summary of the results are as follows:

(a) The type of surfactant and heat treatment affect the size of platinum nanoparticles. For instance, a branched surfactant, tert-octanethiol, causes an increase in the size of platinum nanoparticles compared to linear surfactant, 1-hexanethiol. Moreover, the average size of the platinum nanoparticles increases with increase in the heat treatment temperature (Catalysts I, II, III, IV and Catalysts I, Ia, Ib, Ic, II, IIa, IIb, IIc).

(b) The optimum platinum nanoparticles size is about 3 nm and the Pt (0) to Pt (IV) ratio is about 7 to 3 in catalyzing methanol oxidation reaction (Catalysts I, II, III, IV and Catalysts I, Ia, Ib, Ic, II, IIa, IIb, IIc).

(c) The decrease in the sulfur content of sulfur hydrocarbon increases the active surface area of platinum nanoparticles and decreases the onset potential of the methanol oxidation reaction (Catalysts I, II, III, IV and Catalysts I, Ia, Ib, Ic, II, IIa, IIb, IIc).

(d) The decrease in the electronic charge density on Pt (0) decrease in the performance of catalyst in the methanol oxidation reaction, consequently, the activity of catalyst decreases as the heat treatment temperature increases (Catalysts I, II, III, IV and Catalysts I, Ia, Ib, Ic, II, IIa, IIb, IIc).

(e) The catalysts that have large amount of Ru incorporation ratio into the Pt fcc structure showed higher catalytic activity compared to the others (Catalysts A, B and C).

(f) Ru (VI), such as RuO<sub>3</sub>, Ru (IV) oxide and/or ruthenium (III and/or IV) oxyhydroxide, such as  $RuO_x(OH)_{3-2x}$  and/or  $RuO_x(OH)_{4-2x}$  provide a suitable PtRu surface for the methanol oxidation reaction because of the ability of the ruthenium oxyhydroxide to remove poisoning  $CO_{ads}$  by oxidizing it to  $CO_2$  (g) by bifunctional mechanism. The formation of those ruthenium oxyhydroxide explain why the methanol oxidation reaction starts at more negative potentials and the maximum activity is seen at high potentials (Catalysts A, B and C).

(g) Catalyst A (70 % Pt and 30 % Ru) is the most active catalyst among the prepared catalysts and has almost 6 times higher catalytic activity than commercially available E-TEK catalysts.

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# Fatih Sen (CV)

Research Assistant

Department of Chemistry

Phone: 90 312 210 7615

Mobile: 90 505 918 44 98

e-mail: fsen@metu.edu.tr

Faculty of Arts and Sciences

fax: 90 312 210 3200

Middle East Technical University (METU)

Ankara, Turkey, 06531

# PROFESSIONAL POSITIONS

Turkish Scientific and Research Council (TÜBİTAK) Research Fellow Visiting Scholar in Nanotechnology and Biotechnology at MIT

February 2011- June 2012

Advisor: **Professor Michael S. Strano,** Department of Chemical Engineering at MIT (Massachusetts Institute of Technology)

Carbon Nanotubes- Nano and Biosensors- Bioenergy and Biofuel cells, Thermopower energy systems-Nanocatalysts

Graduate Student Research in Inorganic Chemistry

# September 2004-February 2011

Advisor: **Professor Gulsun Gokagac,** Department of Chemistry at METU (Middle East Technical University)

**PhD Thesis:** Preparation and characterization of carbon supported Pt and Pt+second metal nanoparticle catalysts for methanol oxidation

### **EDUCATION**

PhD candidate in Inorganic Chemistry, METU, Ankara, Turkey 2012

BS in Chemistry, Selcuk University, Konya, Turkey2001

# AWARDS

TUBITAK, Young Scientist Training Program, Research Fellowship (*Nation-wide*)2011-2012

TUBITAK, PhD Fellowship (*Nation-wide*) 2005-2010

Graduation Degree, High Honour student (*Ranked First*) 2001

#### **Research Experience**

**2011-2012** Intra- and inter-cellular signaling pathways that often involve too small molecules to detect using conventional assays and instrumentation were investigated. Moreover, we designed and synthesized fluorescent nanosensors capable of listening to these signals, even at the single molecule level. Our work

focuses on the synthesis and mathematical analysis of these analytical platforms to solve biological problems.

**2011-2012** First reported by the Strano laboratory (our laboratory at MIT) in March 2010, thermopower waves are self-propagating chemical reaction waves guided by a thermally conductive nanotube or nanowire. The large, rapidly moving thermal gradient also pushes charge carriers with it, generating voltage and current. They hold promise as the basis for new types of fuel cells, as well as ultra-high power density batteries, already generating up to 7 W/g. We developed both the theory and the experimental applications of these waves.

**2008-2010** Synthesis, characterization of carbon supported Pt nanoparticle catalysts for direct ethanol fuel cells<sup>4</sup>. Thiol stabilized platinum nanoparticles catalyst was synthesized and characterized via XRD, XPS, TEM-EDX, AFM-STM, FTIR. The effect of the precursor material on the catalytic activity was investigated and it was seen that there were not much effect of the precursor material on ethanol oxidation.

**2005-2008** Preparation and physical/chemical characterization of new carbon supported and non-supported metal nanoparticle catalysts. Carried out XRD, XPS, TEM-EDX, AFM-STM, FTIR, ICP-MS, UV, elemental analysis, SEM, TGA studies on these catalysts; also determined electrochemical catalytic activity for direct methanol fuel cells. The results showed that synthesized metal nanoparticle catalysts were much higher catalytic activity compared to commercial and other catalysts in literature.

**2005-2006** Sythesized and characterized PtRu nanoparticle catalysts for potential applications in direct methanol and ethanol fuel cells. The catalysts were sythesized by superhydride reduction method and characterized via XRD and XPS. TEM,EDX,

AFM and STM were carried out to determine the particle size and content of the catalysts. The effect of Ru in the prepared catalysts is explained through the bifunctional mechanism and the modification of the Pt electronic states.

# **TEACHING EXPERIENCE**

# Graduate Student Instructor METU/September 2010- February 2011

- Supervised Inorganic Chemistry Laboratory for 70 students
- Graded labaratory reports and designed midterm and final exams for Inorganic Chemistry Laboratory

# Graduate Student Instructor METU/September 2006- September 2010

- Supervised Instrumental Analysis Laboratory for 110 students
- Graded labaratory reports and designed midterm and final exams for Instrumental Analysis Laboratory

# Graduate Student Instructor METU/September 2005-September 2006

- Supervised Analytical Chemistry Laboratory for 125 students
- Graded labaratory reports and designed midterm and final exams for Analytical Chemistry Laboratory

# Graduate Student Instructor METU/September 2003-September 2005

- Supervised General Chemistry Laboratory for 75 students
- Graded labaratory reports and exams for General Chemistry Laboratory

# PROFESSIONAL MEMBERSHIP AND ACTIVITIES

2010-2012 Reviewer in Journal of Solid State Chemistry, Journal of Nanoparticle Research and Bulletin of Material Science

# **PUBLICATIONS**

**1. Fatih Sen,** Zachary W. Ulissi, Selda Sen, Ardemis A. Boghossian, Xun Gong, Jingqing Zhang, Luiz C. Godoy, Nicole Iverson, Michael S. Strano

"Single Molecule Detection of Nitric Oxide Using Fluorescent Carbon Nanotubes for in vitro and in vivo studies"

#### Planning to submission to Nature Nanotechnology

 Joel T. Abrahamson, Bernat Sempere, Michael P. Walsh, Jared M. Forman, Fatih Sen, Selda Sen, Sayalee G. Mahajan, Geraldine L. C. Paulus, and Michael S. Strano "Excess Thermopower and Thermopower Waves"

# Planning to submission to PNAS

 Selda Sen, Fatih Sen, Ardemis A. Boghossian, Jingqing Zhang, Michael S. Strano

"The Effect of Reductive Brightening Agents on the Sensitivity of SWNT Florescent Sensors "

Accepted in Journal of Physical Chemistry C

4. Jingqing Zhang, Paul W. Barone, Jong-Ho Kim, Shangchao Lin, Dahua Lin, Daniel A. Heller, Ardemis A. Boghossian, Andrew J. Hilmer, Alina Rwei, Allison C. Hinckley, Mia A. Shandell, Nitish Nair, Steven Blake, Fatih Sen, Selda Sen, Robert G. Croy, Deyu Li, Kyungsuk Yum, Jin-Ho Ahn, Nidhi Shrivastav, George W. Pratt, Ning Gao, Bin Mu, Zachary W. Ulissi, Hong Jin, Jyoti R. Arkalgud, John M. Essigmann, Daniel Blankschtein, and Michael S. Strano
"Molecular Recognition Using Nanotube-Adsorbed Polymer Assemblies: Nanotube Antibodies"

Submitted To Nature

 Fatih Sen, Ardemis A. Boghossian, Selda Sen, Zachary Ulissi, Michael S. Strano

"Oscillatory Surface Reactions of Riboflavin, Trolox and Single Oxygen on Single Walled Carbon Nanotubes Probed by Near Infrared Fluorescence"

### Submitted to ACS Nano

6. Selda Sen, Ardemis A. Boghossian, Fatih Sen, Brenna Gomez, Juan Pablo Giraldo, Michael S. Strano 'Nanoparticle Scavenging of Reactive Oxygen Species in Isolated Chloroplasts from Spinacia oleracea'

# Submitted to Advanced Energy Materials

7. Fatih Sen, Zafer Ozturk, Selda Sen, Gulsun Gokagac

"The preparation and characterization of nano-sized Pt-Pd alloy catalysts and comparison of their superior catalytic activities for methanol and ethanol oxidation "

# In press in Journal of Materials Science

8. Fatih Sen, Salih Ertan, Selda Sen, Gulsun Gokagac

"Platinum nanocatalysts prepared with different surfactants for C1 to C3 alcohol oxidations and their surface morphologies by AFM"

#### J Nanopart Res 2012, 14, 922-26

**9.** Fatih Şen, Selda Şen, Baran Can Sağlam, Özgür Topuz, Gülsün Gökağaç and Güliz Görgül

"Effects of MTAD solution on gutta percha and resilon cones: An Atomic Force Microscopy and SEM study"

#### Submitted To Journal of Endodontics

**10. Fatih Şen,** Selda Şen, Baran Can Sağlam, Özgür Topuz, Gülsün Gökağaç and Güliz Görgül

"Effects of CHX solution on gutta percha and resilon cones: An Atomic Force Microscopy and SEM study"

# Submitted To Journal of Endodontics

11.Özgür Topuz, Baran Can Sağlam, Fatih Şen, Selda Şen, Gülsün Gökağaç and Güliz Görgül

"Effects of sodium hypochlorite on gutta percha and resilon cones: An Atomic Force Microscopy and SEM Study"

### Oral Surg Oral Med Oral Pathol Oral Radiol Endod. 2011, 112(4), e21-6.

12. Fatih Şen, Selda Şen and Gülsün Gökağaç

"Efficiency enhancement in the methanol/ethanol oxidation reactions on Pt nanoparticles prepared by a new surfactant, 1,1-dimethyl heptanethiol, and surface morphology by AFM"

#### Phys. Chem. Chem. Phys., 2011, 13, 1676-1684

#### 13. Selda Şen, Fatih Şen and Gülsün Gökağaç,

"Preparation and characterization of nano-sized Pt–Ru/C catalysts and their superior catalytic activities for methanol and ethanol oxidation"

Phys. Chem. Chem. Phys., 2011, 13, 6784-6792

14. Fatih Şen and Gülsün Gökağaç,

Improving Catalytic Efficiency in the Methanol Oxidation Reaction by Inserting Ru in Face-Centered Cubic Pt Nanoparticles Prepared by a New Surfactant, tert-Octanethiol
## Energy & Fuels, 22 (3), 2008, p.1858-1864.

15. Fatih Şen and Gülsün Gökağaç,

"Different sized platinum nanoparticles supported on carbon: An XPS study on these methanol oxidation catalysts"

## Journal of Physical Chemistry C, 111, 2007, p.5715-5720

16. Fatih Şen and Gülsün Gökağaç,

"The activity of carbon supported platinum nanoparticles towards methanol oxidation reaction – role of metal precursor and a new surfactant, tert-octanethiol"

Journal of Physical Chemistry C, 111, 2007, p.1467-1473.

17. Michael W Pitcher, Yasin Arslan, Pelin Edinç, Mujgan Kartal, Mehdi Masjedi, Onder Metin, Fatih Şen\_Ozlem Turkarslan and Basak Yigitsoy,"Recent advances in the synthesis and applications of inorganic polymer"

Phosphorus, Sulfur and Silicon and the Related Elements 182 (12), (2007), p.2861-2880.

18. Gülsün Gökağaç, Muammer Sonsuz, Fatih Şen and Duygu Kısakürek

"Atom Transfer Rearrangement Radical Polymerization Diammine- bis(2,4,6 trihalophenolato)copper(II) Complexes in Solid State"

Zeitschrift für Naturforschung B, Journal of Chemical Sciences, 61b, 2006, p.1222-1228.

19. Gülsün Gökağaç, Leyla Tatar Yıldırım, Muammer Sonsuz and Fatih Şen

"Spectroscopic and crystal structure analysis of diamminebis(2,4,6-triiodophenolato-O) copper(II) "

Crystal Research and Technology. 41 (5), 2006, p.523-527.

20. Gülsün Gökagaç, Leyla Tatar Yıldırım, Muammer Sonsuz and Fatih Şen

"Spectroscopic, magnetic and crystal structure analysis of diammine-bis(2,6dibromo-4-chlorophenolato-O)copper(II)"

Zeitschrift für Naturforschung B, Journal of Chemical Sciences 60 (5), 2005, p.543-547.