PREPARATION OF Pt/Al_2O_3 FOR PREHEATING SYSTEM ON AUTOTHERMAL REFORMER FOR FUEL CELL

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Date : 15 May 2008

PREPARATION OF Pt/Al_2O_3 FOR PREHEATING SYSTEM ON AUTOTHERMAL REFORMER FOR FUEL CELL

QUSYAIRI BIN ALI

A thesis submitted in fulfillment of the
requirements for the award of the degree of
Bachelor of Chemical Engineering
(Gas Technology)

Faculty of Chemical and Natural Resources Engineering
University Malaysia Pahang (UMP)

MAY 2008

I declare that this thesis entitled "*Preparation Of Pt/Al_2O_3 For Preheating System On Autothermal Reformer For Fuel Cell* " is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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To my parents and all of my family for their love.
All the teachers I have had and
to whom I owe so much

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ABSTRACT

Preheating system for autothermal reformers (ATR) is needed to ensure shorter start-up times due to the heat supplied to the catalyst bed by catalytic combustion of the fuel. Nobel metals such as platinum, have been used as catalysts for the catalytic oxidation of hydrogen and show higher activity. However, the platinum catalyst will involve a very high cost because of the platinum price it self. Accordingly, the preparation of platinum catalyst to an alumina support has been investigated in this study. The sample Pt/Al_2O_3 catalyst was prepared with different platinum weight loading which is 1wt% and 3wt% by impregnation process. hexachloroplatinic acid (H_2PtCl_6) and Gama-alumina (γ-Al_2O_3) solutions were used in this preparation. The hydrazine NH_4 added to reduce the chlorine ion from Platinum during preparation. Procedures and condition of impregnation, drying and calcination was discussed. Catalyst characteristic was analysed using Fourier Transform Infra-Red (FTIR) spectroscopy and Scanning Electron Micrograph (SEM). Comparison with literature FTIR data indicated that platinum was dispersed into γ-Al_2O_3. SEM micrograph show that crystallites structure of platinum was formed at γ-Al_2O_3 surface. In addition, both samples were tested through catalytic combustion of hydrogen at fixed air and fuel ratio. The result shows that the 3wt% of Pt/ γ-Al_2O_3 performance is better than 1wt% of Pt/ γ-Al_2O_3 with the highest temperature of $362^{o}C$. This temperature is enough to supply the heat to the Autothermal reformer catalyst for it to function efficiently.

ABSTRAK

Sistem pra-pemanasan untuk ATR adalah perlu bagi memastikan masa permulaan lebih pendek dengan membekalkan haba kepada bahagian mangkin melalui pembakaran bermangkin. Logam terpilih seperti platinum, telah digunakan sebagai mangkin untuk pengoksidaan bermangkin kepada metana dan menunjukkan pengaktifan tertinggi. Namun demikian, mangkin platinum akan melibatkan cos yang tinggi disebabkan harga platinum tersebut. Sejajar dengan itu, penyediaan mangkin platinum dengan sokongan alumina telah dicadangkn dalam penyelidikan ini. Sampel mangkin Pt/Al_2O_3 telah disediakan dengan berlainan kandungan berat platinum iaitu 1% dan 3% melalui proses *Impregnasi.* Larutan Gama-alumina (γ-Al_2O_3) dengan heksakloroplatinik asid (H_2PtCl_6) telah digunakan dalam penyediaan ini. Hidrazin NH_4 tambah untuk menurunkn ion klorin daripada platinum semasa penyediaan. Tatacata dan kondisi imprignasi, pengeringan dan *Calsinasi* di bincangkan. Ciri-ciri fizikal mangkin diuji dengan menggunakan Perubahan Fourier Sinar Infra-Mareh (FTIR) spektroskopi dan Imbasan Elektron Mikrograf (SEM). Perbandingan dengan kajian FTIR yang lepas, didapati data taburan platinum keatas γ-Al_2O_3 berlaku. SEM mikrograf menunjukkan pembentukan struktur kristal platinum diatas permukaan γ-Al_2O_3. Tambahan pula, kedua-dua sampel di uji melalui pembakaran bermangkin pada nisbah bahan bakar dan udara yang tetap. Keputusan ujian menunjukkan pencapaian 3wt% of Pt/ γ-Al_2O_3 adalah lebih baik berbanding 1wt% of Pt/ γ-Al_2O_3 dengan suhu maksimun adalah 362 darjah selsius. Suhu ini cukup bagi membekalkan haba kepada mangkin ATR untuk berfungsi dengan berkesan.

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LIST OF ABBREVIATIONS

ATR	– Autothermal Reformer
CPO	– Catalytic Partial Oxidation
FTIR	– Fourier Transform Infrared spectroscopy
HTS	– High Temperature Shift
PEMFC	– Proton Exchange Membrane Fuel Cell
SMR	– Steam Methane Reforming
SEM	– Scanning Electron Micrograph
TEM	– Transmission Electron Microscopy

CHAPTER 1

INTRODUCTION

1.1 Background of study

The automobile industry is under a great deal of pressure to produce and market low emission vehicles. Beginning in 2003, 10 percent of vehicles offered for sale in California will be required to be zero-emission vehicles. Other states are also moving toward this objective. (Fuel Cell 2000)

Fuel cells show great promise as a replacement to internal combustion engines in automobiles due to their high efficiency, low or zero emissions, and quiet, continuous operation. The Proton Exchange Membrane fuel cell (PEMFC) has additional advantages because of its low operating temperature, high power density, and advanced stage of technical development. The PEMFC uses hydrogen, which is not easily transported or stored.

For these reasons, and in order to take advantage of the existing fuel infrastructure, the PEMFC needs to be integrated with a fuel processor that can use methane that can be conveniently distributed. Figure 1.1 illustrates the chemical unit operations necessary to process fuel and how the system is integrated with a PEMFC.

In the production of hydrogen, it is well known in the art to treat hydrocarbon material with a catalyst at high temperatures in the presence of steam. Autothermal reforming is an approach that combines catalytic partial oxidation and steam reforming. Partial oxidation employs substoichiometric combustion to achieve the temperature to reform the fuel. Fuel, oxidant (oxygen or air, for example), and steam are reacted to form primarily hydrogen, CO_2 and CO.

An advantage of autothermal reforming technology is that the exothermic combustion reactions are used to drive the endothermic reforming reaction. Autothermal reforming typically employ noble metal catalyst beds operating at temperature of about 870^oC to about 1300^oC. In comparison to steam reformers, and advantage of autothermal reformers is that at these high operating temperatures, sulfur in the fuel, which is present primarily as H_2S, does not significantly poison the catalyst and permit downstream sulfur remover. (Richerd, 2002)

A further advantage of autothermal reformers is that start-up times also tend to be shorter due to the heat supplied to the catalyst bed by catalytic combustion of the fuel.

1.2 Problem statement

Preheating System for autothermal reformers needed to ensure start-up times also tend to be shorter due to the heat supplied to the catalyst bed by catalytic combustion of the fuel.

Catalyst in the preheating system is used to perform catalytic combustion. One of factor that influences the combustion performance is catalyst activity. Nobel metal such as Pt, have been used as catalysts for the catalytic oxidation of methane and show higher activity.

However, the platinum catalyst will involve a very high cost because of the platinum price it self. So, the other alternative is to prepare platinum catalyst are usually dispersed on a support in order to increase cost efficiency. The catalysts are being supported by a highly porous and thermally stable material (such as alumina) onto platinum which the active species are being dispersed to form Platinum Alumina (Pt/Al_2O_3) catalyst. The main purpose of a support is to achieve an optimal dispersion of the catalytically active component(s) and to stabilize it against sintering.

1.3 Objective

The main objectives of this research are:

i) To study the method of preparation Pt weight loading over alumina support catalyst.

ii) To find the optimum temperature by catalytic combustion of hydrogen with fixed air fuel ratio.

1.4 Scope of research

In order to fulfill the objectives, the scopes of the study are:

i) Preparation of Pt/Al_2O_3 catalyst with different weight loading which is 1wt% and 3wt% from hexachloroplatinic acid (H_2PtCl_6) by using impregnation method.

ii) Analysed catalyst characteristic in order to know the dispersed of platinum and the structure of support.

iii) Tested the catalyst through catalytic combustion at fixed air and fuel ratio to get the temperature profile.

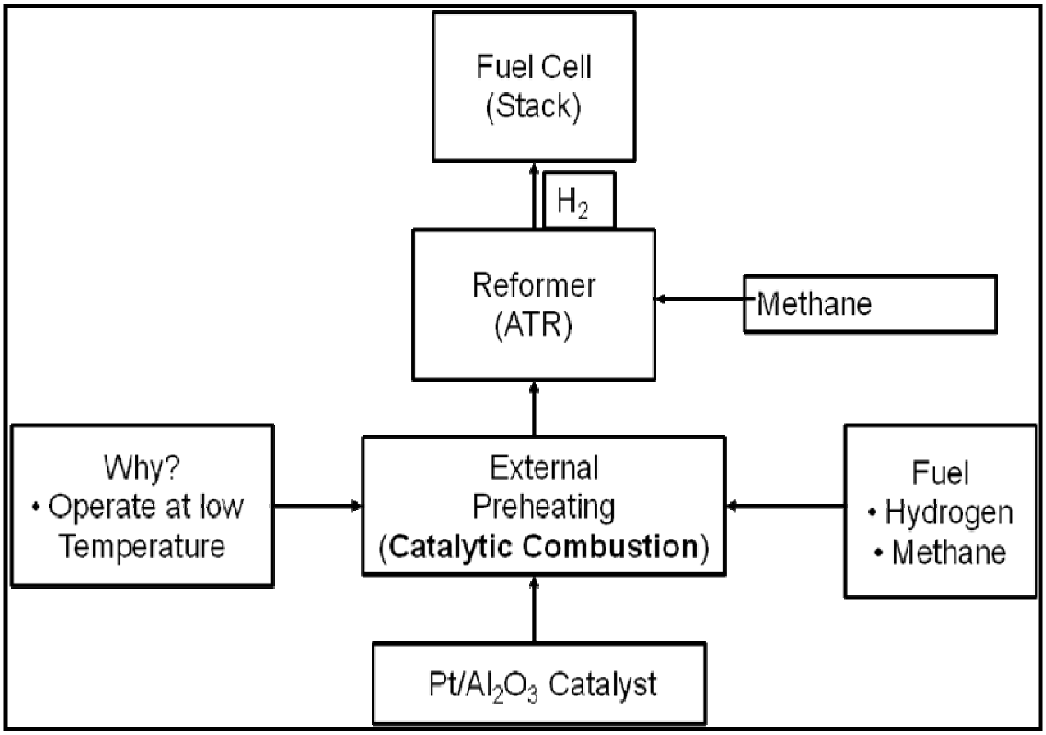

Figure 1.1: Fuel Processor/Fuel Cell System

CHAPTER 2

LITERATURE REVIEW

2.1 Preparation of Platinum Catalyst

Olsbye, et al. (1996) proposed “Impregnation of platinum metal was performed using an aqueous solution of H_2PtC1_6 (Hexahydrat zur Synthese, Merck). The impregnation method basically followed [1], with the following procedure. The impregnation was performed in a shaking waterbath at 20°C under an inert atmosphere (N_2). In order to prevent light promoted dissociation of the complex [2], the experiments were performed in complete dark, with the exception of red light illumination during sampling and work-up. The H_2PtC1_6 solution (0.005M, 150 ml) was added to a three-neck flask. The pH of the solution was initially 2.2. It was adjusted by adding either HCl (1M) or NaOH (1M). The relationship between NaOH addition and pH in the different starting solutions is shown in Table 1. Then the alumina (3 g) was added and the mixture was left with shaking for a given contact time. The pH of the solution was monitored by a pH-meter (Oakton RS232). It should be noted that measurement of pH in the solution caused diffusion of KCl from the electrode into the solution, affecting the Cl-analyses considerably. Samples of the solution (2 ml) were withdrawn using a pipette, filtered (S and S Filter paper circles, 5893 ashless Blue ribbon) and stored in closed sample holders. After completing the impregnation, the solution was filtered from the alumina, and the solid was dried (90°C, 2 h). The catalyst was wet calcined (air saturated with water at 65°C) at 570°C for 120 min., and then further calcined in dry air at 570°C for 60 min.”

Freni, et al. (1999) proposed “The washcoating procedure proceeds through the impregnation of the frame structure by an aqueous slurry of $–Al_2O_3$ of powders190 m^2/g, 2 3 porositys80%-25 mm. and HCl. After impregnation, monoliths are slowly dried, at 100°C, and calcinated at 550°C, under a flow of air. This process can be repeated two or more times in order to enhance the amount of deposited alumina. The most delicate step in the process is the dispersion of the metal salts from which the catalyst will be obtained.”

Ma L., et al. (1995) proposed “A $Pt/\alpha A1_20_3$ catalyst was made in the laboratory. γ-$A1_20_3$ was calcined at 1273K (4 h) to produce a product shown to be mainly &A1203 by X-ray diffraction. The surface area was 130 m 2 g-1. This material was crushed and sieved to 250-500 μm. A calculated amount of chloroplatinic acid was dissolved in water to give a solution of volume ca. 2 × the pore volume of the support. The solid was mixed with the liquid and gently stirred at room temperature for 3 h. The slurry was then dried at 330-343 and 393K overnight. Calcination at 773 K (4 h) was followed by reduction at the same temperature (H_2:4 h). Once the catalyst had been reduced, no further reduction was necessary, even after exposure to air. The catalyst was found to have a BET surface area of 128 m 2 g-I and a metal surface area, measured by CO adsorption and assuming 1" 1 stoichiometry, of 0.35 m 2 g^{-1}.”

Yem, et al. (2007) proposed “Pt/γ-Alumina catalysts were synthesized by impregnation of different supports. The required amount of 8 wt% liquid H_2PtCl_6 dissolved in 50 mL of water was directly impregnated onto the four types of supports. As a rule, the metal loading on the support corresponded to 5 wt%. The temperature was increased to 70°C and the mixture was stirred vigorously in a closed beaker for 3 h. Then, after adsorption equilibrium had been reached, the excess water was removed using a rotary evaporator. The catalyst was then dried overnight in air at 120°C, followed by calcination in a 100 mL/min air flow for 2 h. Reduction was accomplished using a 50 mL/min H2 flow for 2 h at 400°C. The hydrogenation of a mixture of 1-hexene and *n*-heptane at a 1-hexene/*n*-heptane molar ratio of 1:8 was carried out using a fixed bed reactor under continuous flow and atmospheric pressure. The sample amounts used were 0.375 g. The reaction temperature investigated was 30^{o}C. The products were analyzed online by a gas chromatograph equipped with a flame ionization detector."

Shelimov, et al. (1999) proposed "Al_2O_3 (15 g) was added to 250 ml of 0.1 M HCl at pH 1.4, and the mixture was stirred for 4 h until pH 4.0 was reached. The excess HCl was then removed, and 200 ml of 0.1M HCl was added followed by stirring for 3 h until pH 1.7 was attained, decanting, filtering the powder, and drying it at 90^{o}C overnight. A stock (6.6x10^{2} M) H_2Pt_Cl6 solution at pH 1.15 was used for alumina impregnation; it was prepared by diluting a 8 wt% aqueous solution of H_2PtCl_6 (Aldrich) with water. The pH values were measured using a Tacussel PHN-850 digital pH meter. No change in pH was found to occur for the aged stock solution. A less acidic H_2PtCl_6 solution at pH 2.83 also used for alumina impregnation was prepared by adding 1 or 0.1 M NaOH to the stock H_2PtCl_6 solution. This solution was aged for at least 2 days before alumina impregnation. $H_2PtCl_6/\alpha\text{-}Al_2O_3$ samples were prepared by adding the H_2PtCl_6 solution to alumina upon continuous stirring at 20^{o}C. The volume of the impregnating solution was typically twice greater than the alumina pore volume. After impregnation, the samples were first dried in a dessicator over P_2O_5 under vacuum and then in air at 90 and/or 150^{o}C and finally calcined at a higher temperature. The Pt content in the impregnated alumina samples was 1.5 wt%."

Corro, et al. (2005) proposed "The support used was $\alpha\text{-}Al_2O_3$ Merck with a grain size of 0.063–0.200 mm (70–230 mesh ASTM). Before use, the support was calcined for 6 h at 600^{o}C in air. Pt catalyst supported on alumina was prepared by impregnation using acidic aqueous solutions (0.1 M HCl) of H_2PtCl_6 X $6H_2O$ (Merck, min. 98% purity). After impregnation, the catalyst was dried at 120 _C overnight, and then calcined in flowing air for 6 h at 500^{o}C. Finally, the catalyst was reduced in pure hydrogen flow for 8 h at 500^{o}C. A reference alumina support was prepared in the same way using only diluted hydrochloric acid. A sample of the reduced catalyst was then sulfated. Sulfation was performed on the sample heating to 500^{o}C in flowing air (100 cm3 min_1). The feed was then changed at 500^{o}C for a nitrogen flow containing 50 ppm SO2, 5%O2 (100 cm3 min_1) for 10 h. The samples were then cooled to 25^{o}C."

Catalysis Letters 70 (2000) 109–116 proposed “Pt/Al_2O_3 was prepared by the wet impregnation technique. For this purpose, a solution of $H_2PtCl_6 \cdot 6H_2O$ in water (0.01 g Pt / ml) and Al_2O_3 (000–3AQ, AKZO, The Netherlands) were used. The Al_2O_3 was obtained by extruding the gel. The pellets were crushed and sieved to particles with diameters between 0.3 and 0.6 mm. The grains were calcined for 15 h at 1125 K (heating rate 3 K / min) in flowing air (30 ml / min) and subsequently impregnated with Pt (0.5 wt%). The catalysts were dried at 365 K for 2 h in a rotating evaporator followed by drying overnight at 395 K in static air. The impregnated grains were calcined for 15 h at 925 K (heating rate 3 K / min) in flowing air (30 ml/min). The Pt content of the catalysts was determined by atomic absorption spectroscopy.”

Applied Catalysis A: General 255 (2003) 83–92 proposed “The γ-Al_2O_3 support (Harshaw, Al 3996) was calcined in flowing air at 550^oC for 2 h. The ZrO_2 support was prepared by calcination of zirconium hydroxide (MEL Chemicals) using the same conditions. The 10% ZrO_2/Al_2O_3 was obtained by impregnation of alumina with a nitric acid solution of zirconium hydroxide, as described elsewhere [13]. The supports were impregnated with an aqueous solution of chloroplatinic acid (H_2PtCl_6, Aldrich) by incipient wetness technique. The catalysts were subsequently dried overnight at 120^oC and calcined in air at 550^oC for 2 h. The platinum content was around 1 wt. %”

Catalysis Letters Vol. 91, Nos. 1–2, (2003) Proposed “Al_2O_3, ZrO_2 and CeO_2 supports were prepared by calcination of γ-alumina Engelhard Corporation Catalyst), zirconium hydroxide (MEL Chemicals) and cerium ammonium nitrate (Aldrich) at 550^0C for 2 h under flowing air. The platinum catalysts were prepared by incipient wetness impregnation of the supports with an aqueous solution of chloroplatinic acid (H_2PtCl_6, Aldrich), followed by drying at 120^oC for 16 h and calcinations in air at 550^oC for 2 h. All samples contained about 1 wt% of platinum, which was determined by atomic absorption spectrometry. The prepared catalysts are referred to as PtAl for Pt/Al_2O_3, PtZr for Pt/ZrO_2 and PtCe for Pt/CeO_2.”

Applied Catalysis B: Environmental 75 (2007) 59–70 proposed “Preparation of the catalyst-precursor: the support was a commercial γ-Al2O3 (Alfa Aesar, 99.97%; grain size = 3 mm) dispersed in water (1 l of distilled water per 4 g of g-Al_2O_3) and then impregnated with an aqueous solution (1 M) of $(NH_3)4Cl_2.H_2O$ (M = Pd, Pt; Aldrich, 99.99+%), the final pH is adjusted at 10.6 by adding ammonia solution (NH_4OH 25%, Fisher Scientific) dropwise; once the solvent has been evaporated at a reduced pressure in a rotavapor at 323 K, the solid is allowed to dry overnight at 383 K (the weight percentages of Pt-Pd are listed in Table 1); the catalysts are denoted as Pt(x)-Pd(y)/g-Al_2O_3, where x and y are the weight percentages of platinum and palladium, respectively.”

2.2 Preparation of Noble Metal Catalyst

Nohaira, et al. (2005) proposed “The various supports were ground and then sieved to retain particles with sizes between 0.10 and 0.04 mm. The monometallic Pd based catalysts were prepared either via cationic exchange of the support (SiO_2) by Pd $(NH_3)4(NO_3)2$ in basic medium (pH = 11) or via simple impregnation (Al_2O_3, TiO_2, MgO, ZnO, CeO_2, $CeZrO_2$) using the same Pd precursor. The monometallic catalysts were dried overnight at 120 ◦C, then calcined in flowing air at 300°C for 4 h, and finally reduced under hydrogen flow at 400°C for 4 h. The Pd/TiO_2 catalyst was reduced at 300°C instead of 400°C in order to avoid the SMSI effect. Bimetallic Pd–Pb catalysts were prepared by the surface redox reaction between hydrogen activated on palladium particles and the lead precursor ($Pb(CH_3COO)_2$) dissolved in methanol (“catalytic reduction” method [26]). This preparation method of bimetallic catalysts is well known to induce a strong interaction between the two metals whatever the prepared bimetallic system [27–29]. A known amount of the prereduced palladium catalyst was introduced into a reactor under nitrogen and was activated at 300°C for 1 h under hydrogen. Then the solution of the lead precursor in methanol, previously degassed under nitrogen flow, was introduced onto the catalyst at room temperature. After a 1 h reaction time under hydrogen bubbling, the solution was filtered out and the catalyst was dried overnight at 100°C. Finally, the bimetallic catalysts were reduced under hydrogen flow at 300°C for 2 h (2 ◦C/min heating rate).

Using the same approach, a blank Pd catalyst over SiO_2, named "Pd1 treated in CH_3OH/H_2" further in the text, was also prepared in a methanol solution without addition of the lead precursor."

Tichit, et al. (2007) proposed "The initial Mg/Al/NO_3 LDH was prepared by coprecipitation at constant pH (_10) of aMg and Al nitrates solution (Mg/ Al: 0.75/0.25) with a solution of NaOH (1.0 M). The addition rate of the alkaline solution and the pH were controlled by using a pH-STAT Titrino (Metrohm) apparatus. The suspension was stirred overnight at 353 K for 17 h, and then the solid was separated by centrifugation, rinsed thoroughly with distilled water (Na < 100 ppm) and dried overnight at 353 K. The Mg(Al)O mixed oxide support was then obtained by activation of Mg/Al/NO3 LDH in air-flow at 773 K for 3 h (heating rate: 3 Kmin_1). Mg(Al)O was impregnated with Pd acetylacetonate (Pd(acac)2, Aldrich) in water-free toluene solution for 12 h. After solvent evaporation the solid was dried at 353 K in vacuum, calcined for 3 h in air flow at 773 K, then reduced with H2/N2 (10/90, v/v) at 523 K for 5 h (heating rate: 1 K min_1)."

Kurzina, et al. (2006) said "For the study on the influence of the support nature on the catalytic performances of the catalysts, the catalysts were prepared by impregnation of the different supports (a-Si3N_4, b- Si3N_4, SiN-am and SiN-annl) with adequate amounts of Pd(II)- bis-acetylacetonate $[Pd(C_5H_7O_2)_2]$ dissolved in toluene. For the study on the influence of the solvent used in the preparation method on the catalytic performances of the catalysts, these were prepared by impregnation of a-Si3N4 with adequate amounts of Pd(II)-acetate $[Pd(CH_3CO_2)_2]$ dissolved either in toluene or in water. In both cases, we used an excess of solvent. After impregnation, evaporation of the solvent and drying, the catalysts precursors were decomposed under argon flow at 500°C for 2 h. They were then calcined during 2 h at 350°C under oxygen flow and further reduced under hydrogen flow at 500°C (in both cases the heating rate was 1 K min^{-1}). The content of Pd is always 0.5% in weight."

Ji-Jun, et al. (2007) proposed "Pd-B/γ-Al2O3 amorphous alloy catalyst was prepared by the following procedures. γ-Al2O3 powders (Tianjin Chemical Engineering Design Institute, 100–120 mesh) calcined at 550°C for 2 h were impregnated with diluted $PdCl_2$ (Xian Kaili Chemical Engineering Company) solution. The initial amount of Pd was defined as 0.4 wt.% for all the experiments. After dried at 120°C for 2 h, the catalysts were pre-calcined at defined temperature for another 2 h. Then they were reduced by adding KBH4 solution (0.2 M) under gentle stirring in an ice water bath for about 30 min until no obvious bubbles were observed. The resulting black solid powders were washed thoroughly with oxygen-free distilled water until no Cl– ions were detected in the solution and subsequently with pure alcohol. Thermal annealing was carried out in N_2 atmosphere at defined temperature for 2 h. For X-ray diffractive (XRD) characterization, MCM-41 (Tianda Beiyang Company) was used as the support to avoid the diffraction peaks of Pd being overlapped by those of support. For the purpose of comparison, traditional 0.4 wt. % Pd/γ-Al_2O_3 catalyst was prepared by routine impregnation followed with H_2 reduction at 300°C for 2 h."

Shetian, et al. (2003) proposed "The Pd/ZnO catalysts were prepared by either impregnation (IMP series) of a ZnO support (Sakai Co.) with $Pd(NO_3)_2$ aqueous solution (10% $Pd(NO_3)_2$ in 10% HNO3 from Aldrich) or by co-precipitation (CP series) of $Zn(NO_3)_2$ + $Pd(NO_3)_2$ with NaOH + Na_2CO_3 aqueous solutions at constant pH and room temperature. $Zn(NO_3)_2{\cdot}6H_2O$, NaOH, and Na_2CO_3 of analytical grade were from wako chemicals. Pd weight loading for IMP samples was 1–10%, and the nominal Pd loading of CP samples was 1–15%. Thecatalysts were named according to their preparation method and nominal Pd loading. For example, the sample prepared by IMP method with 3.5% Pd was designated as IMP3.5, and the sample prepared by CP method with 15% Pd was designated as CP15, and so on. All the samples were finally calcined at 450 ◦C for 2 h and crushed to 0.15–0.25mm for activity test."

Benkhaled, et al. (2006) Proposed "The preparation method used an aqueous solution of palladium nitrate (Herau¨ s) and a defined quantity of NaNO2 (Aldrich 99.99%), corresponding to a molar ratio NO2/ Pd = 4. Incipient wetness impregnations were realized in a rotating beaker. After drying at 393 K, the catalyst was calcined under airflow at 473 K during 2 h and finally reduced under hydrogen flow. In order to remove residual Na, a washing step with water was performed. FTIR and thermogravimetric analysis of Pd[NO2] catalysts were performed on samples before the washing step. These catalysts are here referred as Pd[NO2]nw (as ‘‘not washed’’ samples). The palladium loading was varied from 0.1 to 0.6 wt.% and two types of alumina support were used: a d-Al2O3 (specific surface area SBET = 130 m2/g and porous volume Vp = 1.04 cc/g), and a gc-Al2O3 (SBET = 200 m2/g, Vp = 0.6 cm3/g). These catalysts are labeled here as 130 or 200Pdx (1 < x < 5). In order to make a comparison, two others catalysts have been prepared starting from bis-acetylacetonate (Strem 99%) in organic medium. The desired amount of $Pd(C_5H_7O_2)_2$ is dissolved in 300 ml of toluene and added to 20 g of α-Al_2O_3 (referred as 130Pd[acac]) or γ- Al_2O_3 (200Pd[acac]) for 72 h at room temperature under stirring. The mixture is then filtered and washed 3 times with 100 ml of distilled water. After drying at 393 K during 12 h, the catalyst is finally calcined in an air flow at 623 K during 2 h.”

Wang, et al. (2007) Proposed “The Rh-based catalysts were prepared by impregnation followed by drying at 110ºC for 12 h and calcination at 500ºC for 2 h in air. All Rh contents were 1% (Rh/Ce molar ratio = 1.2). Prior to the pulse reactions, the catalysts were reduced in H_2 (20 ml/min) at 500ºC for 0.5 h and then heated to 700ºC in Ar. A CH_4 pulse (300.58 μl) was passed over the catalyst and the effluents were analyzed by a gas chromatograph equipped with a TCD. In situ CO-FTIR and Py-FTIR experiments were carried out on a Bruker Equinox 55 Fourier spectrometer.”

James, et al. (2006) proposed”γ -Al_2O_3 (UOP LaRoche VGL-15) was used for preparing 20 wt% CeO_2–Al_2O_3 (Ce–Al) by wet impregnation of $Ce(NO_3)_2$ followed by calcination at 550^{o}C. For the Rh loading, $Rh(NO_3)_3$ was wet-impregnated onto the prepared Ce–Al support. Our preliminary work indicated that the Rh catalyst derived from $Rh(NO_3)_3$ was better than that derived from RhCl3 in terms of better metal dispersion and improved catalyst activity for reforming. The impregnated catalyst was then dried at 100^{o}C overnight, followed by calcination at 550^{o}C, for a nominal Rh loading of 2 wt% for all catalysts studied. For the Rh–Ni bimetallic catalysts, unless described otherwise, the Ni and Rh were co-loaded via wet co-impregnation using a solution of the respective metal nitrates, then dried overnight at 100^{o}C, followed by calcination at 550^{o}C. Several control catalysts were prepared with a different support (the γ -Al_2O_3 without CeO_2) using the same impregnation procedure."

Duprez, et al. (2003) proposed "The support used was a high-surface-area ceria (HSA) provided by Rhodia Rare Earths (BET area, 60 m2 g−1; grain size, about 50 µm; no internal porosity; main impurity, La ≈ 2000 ppm). In order to avoid possible sintering of the oxide during the pretreatment of the catalyst, the support was pretreated at high temperature before impregnation: reduction under H2 at 900°C followed by calcination under air at 450°C. The BET surface was then reduced to 23 m^2 g^{-1}. The catalyst was prepared by impregnation of the pretreated support (5 g) with an aqueous solution of rhodium III nitrate $Rh(NO_3)_3$ from Fluka. The slurry was gently shaken at room temperature on an oscillating table for 16 h. The supernatant solution was evaporated to dryness on a sand bath maintained at 60°C. The catalyst batch was subsequently dried at 120°C and calcined in an air flow at 450°C for 4 h before storage. After impregnation, the metal content was 3.7 wt% in rhodium."

2.3 Summary of Catalyst Preparation

Table 2.2 show the summary on catalyst preparation of platinum alumina. There have ten articles on past research explain the condition during preparing step using impregnation method. Table 2.3 then show the preparation condition of noble metal catalyst using a various method.

Table 2.2: Preparation of Platinum Alumina by Impregnation Method

Article	List of Chem.	stir	pH measure	dry	calcine	Reduction
Unni Olsbye 1996	H_2PtC1_6 (Merck). HC1 (1M) or NaOH (1M). alumina	20°C under an inert atmosphere	pH of the solution was initially 2.2. It was adjusted by adding either HC1 (1M) or NaOH (1M)	90°C, 2 h	(air saturated with water at 65°C) at 570°C for 120 min., and then further in dry air at 570°C for 60 min.	
S. Ereni 1999	H_2PtC1_6 γ-Al_2O_3 HC1			at *T* =100°C	at *T*=550°C under a flow of air	
D.L. Trimm 1995	γ-Al_2O_3 chloroplatinic acid (CLA)	at room temperature for 3 h		330-343 and 393K overnight.	773 K (4 h) was followed by	reduction at the same temperature (H2:4 h)
Jai Neung Kim 2007	liquid H_2PtC1_6 four types of supports	70°C for 3 h		overnight in air at 120°C	in a 100 mL/min air flow for 2 h.	accomplished using a 50 mL/min H2 flow for 2 h at 400°C.
Boris Shelimov 1999	Al_2O_3 0.1 M HC1 0.1 M NaOH H_2PtC1_6 solution	=20°C	mixture was stirred for 4 h until pH 4.0 was reached	desiccators over P_2O_5 under vacuum and then in air at 90 and/or 150°C	at a higher temperature	

Article	List of Chem.	stir	pH measure	dry	calcine	Reduction
Grisel Corro 2005	γ-Al2O3 (Merck) 0.1 M HC1 H_2PtC1_6*$6H_2O$ nitrogen		by impregnation using acidic aqueous solutions	at 120°C overnight	flowing air for 6 h at 500°C	hydrogen flow for 8 h at 500°C (sulfation) nitrogen flow containing 50 ppm SO2, 5%O2 (100 cm3 min_1) for 10 h.
Catalysis Letters 70 (2000)	H_2PtC1_6*$6H_2O$ (0.01 g Pt / ml) Al_2O_3			365 K for 2 h in a rotating evaporator And drying overnight at 395 K	15 h at 925 K (heating rate 3 K / min) in flowing air (30 ml/min).	
General 255 (2003)	γ-Al_2O_3 support (Harshaw, Al2O3, 1996) nitric acid (H_2PtC1_6 , Aldrich)			overnight at 120 °C	550 °C for 2 h in air	
Catalysis Letters Vol. 91, 2003	(H_2PtC1_6 , Aldrich), Al_2O_3, ZrO_2 and CeO_2			120 °C for 16 h	550 °C for 2 h in air	
Applied Catalysis Environmental 75 (2007)	γ-Al_2O_3 $(NH_3)_4Cl_2$*H_2O NH_4OH(1 M)	rotavapor at 323 K	pH is adjusted at 10.6 by adding ammonia solution (NH_4OH 25%, Fisher Scientific) dropwise	overnight at 383 K		

Table 2.3: Preparation of Noble metal Catalyst by Various Method

Article	List of chem.	Stir	pH measure	Dry	Calcine	Reduction
Bendaoud Nohaira 2005	$Pd(NH_3)_4(NO_3)_2$ Al_2O_3, TiO_2, MgO, ZnO, CeO_2, $CeZrO_2$			overnight at 120 °C	in flowing air at 300 °C for 4 h	under hydrogen flow at 400 °C for 4 h
Bendaoud Nohaira 2005 Didier Tichit 2007	Mg and Al nitrates solution NaOH (1.0 M). Pdacetylacetonate ($Pd(acac)_2$, Aldrich)	overnight at 353 K for 17 h	rinsed thoroughly with distilled water (Na < 100 ppm)	overnight at 353 K	In air-flow at 773 K for 3 h (heating rate: 3 Kmin_1).	with H2/N2 (10/90, v/v) at 523 K for 5 h (heating rate: 1 K min_1).
F.J. Cadete Santos Aires 2006	a-$Si3N_4$, b- $Si3N_4$, SiN-am and SiN-anml $Pd(C5H7O_2)_2$			under argon flow at 500^0C for 2 h	2 h at 350^0C under oxygen flow	under hydrogen flow at 500^0C (in both cases the heating rate was 1 K min_1)
Ji-Jun Zou 2007	γ-Al_2O_3 powders $PdCl_2$			dried at 120 °C for 2 h	550 °C for 2 h	adding KBH4 solution(0.2M)under gentle stirring in an ice water bath for about 30 min
M. Benkhaled 2006)	palladium nitrate $NaNO_2$	rotating beaker		drying at 393K	under airflow at 473 K during 2 h	Under hydrogen flow.

Article	List of Chem.	stir	pH measure	dry	calcine	Reduction
WANG Rui1 2007	1% (Rh/Ce molar ratio = 1.2).			drying at 110°C for 12 h	calcination at 500°C for 2 h in air	H2 (20 ml/min) at 500°C for 0.5 h and then heated to 700°C in Ar.
James J. Strohm 2006	Ce(NO$_3$)$_2$ γ -Al2O$_3$			dried at 100 °C overnight	calcination at 550 °C	
Farida Sadi 2003	Rh(NO$_3$)$_3$			dried at 120°C	calcined in an air flow at 450°C for 4 h	reduction under H2 at 900°C
R. Burch 1997	alumina NH$_4$[Fe(EDTA)]			at 120°C overnight	air calcination at 500°C for 4 h in a muffle furnace	

CHAPTER 3

FUEL CELL SYSTEM FOR VEHICLES

3.1 Fuel Cell Stack

There are several types of fuel cells, but Proton Exchange Membrane Fuel Cells (PEMFC) are believed to be the best type of fuel cell as the vehicular power source to eventually replace the gasoline and diesel internal combustion engines. First used in the 1960s for the NASA Gemini program, PEMFCs are currently being developed and demonstrated for systems ranging from 1W to 2kW. (Department of Energy)

PEMFC use a solid polymer membrane (a thin plastic film) as the electrolyte. This polymer is permeable to protons when it is saturated with water, but it does not conduct electrons.

The fuel for the PEMFC is hydrogen and the charge carrier is the hydrogen ion (proton) as shown in Figure 3.1. 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.

Oxygen, usually in the form of air, is supplied to the cathode and combines with the electrons and the hydrogen ions to produce water. The reactions at the electrodes are as follows:

Anode Reactions: $2H_2 \Rightarrow 4H+ + 4e-$

Cathode Reactions: $O_2 + 4H_2 + 4e- \Rightarrow 2 H_2O$

Overall Cell Reactions: $2H_2 + O_2 \Rightarrow 2 H_2O$

Compared to other types of fuel cells, PEMFCs generate more power for a given volume or weight of fuel cell. This high-power density characteristic makes them compact and lightweight. In addition, the operating temperature is less than 100ºC, which allows rapid start-up. These traits and the ability to rapidly change power output are some of the characteristics that make the PEMFC the top candidate for automotive power applications.

Other advantages result from the electrolyte being a solid material, compared to a liquid. The sealing of the anode and cathode gases is simpler with a solid electrolyte, and therefore, less expensive to manufacture. The solid electrolyte is also more immune to difficulties with orientation and has fewer problems with corrosion, compared to many of the other electrolytes, thus leading to a longer cell and stack life.

One of the disadvantages of the PEMFC for some applications is that the operating temperature is low. Temperatures near 100ºC are not high enough to perform useful cogeneration. Also, since the electrolyte is required to be saturated with water to operate optimally, careful control of the moisture of the anode and cathode streams is important.

3.2 Autothermal Reformer (ATR)

Among all the methods that fuel processor, autothermal reforming reaction (ATR) is considered to be one of the most effective processes. This innovative fuel process method consists of two traditional reactions: catalytic partial oxidation

(CPO) and steam methane reforming reaction (SMR). In order to understand the fundamental behavior of ATR, it is essential to understand the characteristics of each process as well.

3.2.1 Catalytic Partial Oxidation

$CH_4 + 1/2O_2 \rightarrow CO + 2H_2$ $\Delta h = -36$ MJ/kmol CH_4 (exothermic)

Catalytic partial oxidation reaction is a less accepted commercial process to produce hydrogen. It is an exothermic reaction that consists of reacting methane with oxygen. The advantages of this reaction are that it has a quick response time, high reaction efficiency and can generate hydrogen without a catalyst.

In addition, the heat it produces usually can be transferred to a heat exchanger for other applications. Nevertheless, the disadvantages of this process are that it requires a high operating temperature, a high fuel/air ratio to precede the combustion reaction, and at the end of reaction, the heat of the waste gas stream cannot be reused, resulting in poor overall energy efficiency. (Jin, 2004)

3.2.2 Steam Methane Reforming

$CH_4 + H_2O \rightarrow CO + 3H_2$ $\Delta h = 206.16$ kJ/mol CH_4 (endothermic)

Majority of hydrogen produced in North America today is produced from steam reforming reaction. The process of this reaction is to combine steam with light hydrocarbon feedstock (in this case methane) in a high temperature and pressure vessel. Since this is an endothermic reaction, usually an enormous amount of heat is required to maintain the temperature in the reactor. To solve this problem, one of the methods that industries apply is to produce heat by burning the feedstock or methane remaining in the waste gas and exchange the heat back to the vessel. With the use of nickel catalyst tubes or beds, the reaction can perform at a faster and more efficient rate.

The advantages of this reaction are that it can achieve energy efficiency as high as 85% with optimal waste heat recovery and can achieve the reaction efficiency of 80%. The main drawbacks of this process are its plant size, slow starting time, and high sulphur content. (Jin, 2004)

The process of ATR uses methane or liquid hydrocarbons as fuel that undergoes a reaction with steam or air in a single reactor. Since the ATR process consists of the combination of CPO and SMR, the balance of the specific heat for each reaction becomes a very distinctive characteristic of this process.

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \qquad \Delta h = -36 \text{ MJ/kmol } CH_4 \text{ (exothermic)}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta h = 206.16 \text{ kJ/mol } CH_4 \text{ (endothermic)}$$

This makes the whole process relatively more energy efficient since the heat produced from CPO can transfer directly to be used by SMR. Under an ideal operating condition with the precise amount of air, fuel and steam, the reaction's theoretical efficiency can even reach higher than conventional SMR process (93.9% vs. 91.7%).

With ATR technologies, conventional SMR plants can be improved by size and weight reduction, lower costs, faster starting time and improved transient-time. Furthermore, the ATR process is capable of using heavy hydrocarbons such as gasoline and diesel, which can make it more appealing marketwise.

Due to the fact that ATR is the least developed process when compared to CPO and SMR processes, numerous scientist and engineers are putting all their effort into the development of this process. One of the more promising results is that by reducing allowable oxygen to carbon ratios and using newly developed catalysts, the operating temperature of the process is greatly reduced from the traditional operating temperature of 1,200°C to 650-900°C. However, the problem of the development of ATR is that although it has a higher theoretical efficiency than the SMR, actual experiment results are still indicating SMR is more efficient. (Jin, 2004)

3.3 Preheating System

The catalytic combustion of methane in autothermal reformer is necessary to initiate oxidation at quite a high temperature. The light-off temperature of methane at an air: fuel ratio of 5.3 is 368°C. Once the reaction starts, subsequent oxidation is rapid and the heat release is considerable. As a result, it is more difficult to control temperature below the desired maximum. (Trimm, 1993)

Preheating system for autothermal need to ensure shorter start-up time due to the heat supplied to the catalyst bed by catalytic combustion of hydrogen. The chemical reaction of oxidation hydrogen gas to water vapor occurs by mixing with oxygen. The chemical reaction is pure (flameless) catalytic combustion of the hydrogen in air and at the surface of a Pt/Al_2O_3 catalyst.

The measured gas and surface temperatures where this combustion occurs range from room temperatures (15°C to 20°C) up to about 500°C. The heat (of combustion) released by the reaction is transferred to the catalyst bed to be heated by conduction and natural connection. (Pangborn, 1981)

3.4 Catalytic Combustion

Catalytic combustion offers an alternative means of producing energy. A wide range of concentrations of hydrocarbon can be oxidized over a suitable catalyst, and it is possible to work outside the flammability limits of fuel. Reaction conditions can usually be controlled more precisely, with reaction temperatures being maintained below 1600°C. This may be important both to minimize the production of nitrogen oxides (NO_x) and also to avoid thermal sintering of the catalyst.

With natural gas, it is somewhat easier to control temperature, since the presence of overall amounts of higher hydrocarbons allows initiation of oxidation at lower temperatures. Thus, for example, the light-off temperature of methane at an air: fuel ratio of 5.3 is 368°C; for ethane, the corresponding value is 242°C (Trimm, 1993)

Once the higher hydrocarbon starts to oxidize, the heat liberated is sufficient to heat up the system and to initiate the oxidation of methane. Obviously, this depends on the fact that there is sufficient higher hydrocarbon to supply the heat required.

The combustion of methane can produce carbon dioxide or carbon monoxide, depending on the air: methane ratio:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (3.1)$$

$$CH_4 + 3/2O_2 \rightarrow CO + 2H_2O. \qquad (3.2)$$

Other reactions may also be involved to a greater or less extent. These could include steam reforming (3.3) and (3.4) and the water gas shift (3.5) reactions:

$$CH_4 + H_20 \rightarrow CO + 3H_2, \qquad (3.3)$$

$$2\ H_2 + O2 \rightarrow 2\ H_20, \qquad (3.4)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2. \qquad (3.5)$$

It will be shown that the most effective catalysts are based on precious metals and over such systems steam reforming becomes important at temperatures in excess of 550^{o}C well within the range of catalytic combustion.

The general pattern of catalytic combustion of hydrocarbons is well established (Figure 3.2). As temperature is increased, oxidation is initiated at a temperature that depends on the hydrocarbon and the catalyst. A further increase in temperature leads to an exponential increase in rate (area B in Figure 2) to the point where heat generated by combustion is much greater than heat supplied. The reaction becomes mass transfer controlled (area C) until the reactants are depleted (area D in Figure 3.2).

One important factor in the catalytic combustion of hydrocarbons is ‘light off’. This can be defined in various ways but refers to the temperature at which mass transfer control becomes rate controlling. Because of the shape of the curve, (Figure 3.2) the definition of light-off temperatures as the temperature at which conversion reaches l0%, 20% or 50% makes little difference.

It is also seen that the kinetics of catalytic combustion are only relevant to parts A and B of Figure 3.2. Once light-off occurs, mass and heat transfer are the important parameters. The geometry of the catalytic combustor together with the porosity of the catalyst/support has much more effect in this region.

The reaction rapidly approaches complete conversion of one or both reactants (Figure 3.2), and the heat generated from the combustion results in a significant increase in catalyst temperature. Thus, the stability of catalysts at high temperatures is also of considerable interest. It is possible to design devices in which efficient heat transfer is used to minimize temperature rise (e.g. the catalytic boiler) but particular attention must be paid in all cases to the temperature stability of materials.

Thus, it is clear that considerations of catalytic combustion must include the chemical reactivity of the catalyst and the hydrocarbon (areas A and B), mass and heat transfer effects (area C) and maximum temperatures reached (relevant to area D). In some cases, further complexity may result from the initiation of homogeneous combustion by overheating the catalyst. (Pfefferle, 1994)

The present article considers mass and heat transfer effects only briefly, but relevant references are provided. Rather, attention is focused on the oxidation of methane on various catalysts in the absence and presence of supports.

3.5 Catalyst Preparation

Catalyst preparation is an important part for metal of applying a catalyst to a support. One of factor that influences the catalytic combustion performance is catalyst activity. The preparation of catalyst is always consider on the effect of metal weight loading and the type of catalyst support to achieve high catalyst activity.

3.5.1 The Effect of Catalyst Performance Base on Metal Weight Loading

Metal oxides and noble metals such as Pt, Rh and Pd have been used as catalysts for the catalytic oxidation of methane. Noble metal catalysts show higher activity than metal oxide catalysts. (Trimm, 1993)

They can be used either with or without a support, but supported catalysts are favored for the oxidation. One particular advantage of supported metal catalysts is that the metal is dispersed over a greater surface area of the support and shows different activity from the unsupported metals due to interactions of the metal with the support. The support also reduces thermal degradation.

The application of noble metals other than Pt and Pd in catalytic combustion is limited practically because of their high volatility, ease of oxidation and limited supply. Palladium and platinum have been the most widely used catalysts for the catalytic oxidation of methane.

The oxidation of methane over various catalysts has been studied by many researchers. Some of the previous results are represented in Table 3.1. The oxidation of methane has been studied using catalysts based on both noble metals and metal oxides such as Co_3O_4, Co,O/alumina, CuO/alumina and CeO/alumina. (Lee, 1994)

The Co_3O_4 catalyst was the most active metal oxide catalyst, but the activity was much less than Pd/alumina catalysts (Table 3.1). Various perovskite-type oxides have also been tested for the catalytic oxidation of methane.

The highest activity metal oxide catalyst was La 0.6 Sr, 4Mn03, which showed similar activity to Pt/alumina catalyst at a conversion level below 80%. However, unlike the Pt/alumina catalyst, the increase in activity with increasing temperature was significantly suppressed at high conversion levels.

During the catalytic oxidation of methane, it was observed that some carbon was deposited on the catalysts. This carbon has almost no effect on the activity of the catalysts, and it was found that the rate of methane oxidation was independent of the deposition of carbon on Pd catalysts. It was reported that the deposition of carbon on Pt catalyst first reduced activity but that this recovered in 15 min. (Lee, 1994)

The effect of Pt loading on the support on the oxidation of methane was investigated. For conversions of methane less than 10%, the oxidation rate of methane increased with an increase in Pt loading over the range of 0.1-2.0 wt% (Trimm, 1994) Similarly, an increase in Pt loading (2.7-10 wt%) on γ-$A1_2O_3$ increased the overall rate of methane oxidation.

However, although the increase in the overall rate of methane oxidation was observed, the activity per unit metal surface area decreased with an increase in loading. (Lee, 1994)

3.5.2 Properties of Catalyst Support

Noble metals are usually dispersed on a support in order to increase cost efficiency. In addition to dispersing the metal, the support acts to stabilise thermally the catalyst and, in some cases, may be involved in the catalytic reaction.

Several types of substrates may be used: these include pellets, wires, tubes, fibre pads and monoliths. Monoliths are mainly used for catalytic combustors in order to obtain high geometric areas of the catalyst and low pressure drop through the system. The choice of monolith material is made on the basis of physical and chemical properties such as surface area, porosity, thermal stability, thermal conductivity, reactivity with reactants or products, chemical stability and catalytic activity.

Metal alloys, which are made of iron, chrome and aluminium, provide excellent mechanical properties and a thinner cell wall, but their thermal stability is not as high as ceramics. Therefore, ceramics have been used far more than metal alloys in the past. The most common high temperature ceramics are based on Alumina (Al_2O_3) (Nielsen, 1984) which is relatively inexpensive and reasonably resistant to thermal shock.

For catalytic combustion, a high surface area is required. Hence, there is a need to increase the low surface areas of the monolith structure. This can be achieved by covering the substrates with a porous layer of ceramic material, which is called a washcoat. The washcoat is coated on the substrates to provide a high surface area. The most commonly used washcoat material is gamma-Alumina (γ-$A1_2O_{3)}$, the surface area of which is quite high.

In catalyst structure, the support plays an important part in determining the activity and long-term stability of the catalysts (Trimm, 1994). The dispersion of Pt on supports was found to be proportional to the activity of catalysts.

It was found that the support material had a strong effect on determining the life of the catalyst. The oxidation of methane was studied over Pt catalysts supported on porous and non-porous alumina fibre (Lee, 1994). Activity of Pt/Al_2O_3 (porous) catalyst was constant for at least 100 h, while the oxidation of methane over Pt/Al_2O_3, (non-porous) gave a variation in products after only approximately 40 h with a constant rate of methane consumption.

3.6 Catalyst preparation method

Many methods have been applied to the preparation of carbon-supported fuel cell catalysts. If we restrict the discussion to the preparation of Pt-based fuel cell catalysts, five general methods have been employed:

i) Impregnation
ii) Ion exchange
iii) Precipitation

3.6.1 Impregnation

The simplest method of preparation is impregnation. In this method, a solution of metal salt(s) is prepared and mixed with the carbon support. The resulting slurry is dried to remove the solvent and then usually heat-treated and/or reduced to decompose the salt to give the desired form of the catalyst. A variation of this method is incipient-wetness impregnation. Here the volume of the impregnating metal solution is chosen to match the pore volume of the carbon. This method has the advantage that metal is only deposited within the pore structure of the carbon.

Numerous examples exist where impregnation has been used to deposit second metals onto a preformed Pt catalyst, followed by the appropriate heat treatment to induce interaction. In the original work by UTC, a preformed Pt catalyst was slurred with aqueous solutions of the second metal and the pH adjusted sufficiently to allow adsorption of the metal onto the catalyst (Jalan, 1980).

However, in general, impregnation is not favored as a large-scale preparation method due to difficulties associated with dry mixing of carbon blacks and the poor wetting of carbons by aqueous solutions.

3.6.2 Ion Exchange

Ion-exchange methods are appropriate for catalyst supports with a large number of ion-exchange sites. However, in general, carbon blacks do not have enough sites to allow sufficient Pt loadings to be achieved. Carbons can be treated to induce further ion-exchange sites to increase Pt loadings, but this is done at the expense of corrosion resistance of the carbon (Stonehart, 1977).

3.6.3 Precipitation

The majority of methods used for the preparation of Pt-based catalysts in the patent literature are based on precipitation. These are generally based on the precipitation of a soluble species by chemical transformation. This can be in the form of a change in pH (e.g., from acidic to basic) or the addition of a reducing agent (e.g., formaldehyde to precipitate metal).

3.6.4 Large-Volume Manufacture of Catalysts

The large-scale manufacture of fuel cell catalysts has a number of important criteria. As well as engineering the ideal nano-scale properties for good performance, such as metal dispersion and alloy formation, large-scale methods must also consider such features as high yield, reproducibility, and ease of manufacture (including health and safety requirements). In general, large-scale production processes are based on precipitation chemistry in aqueous media, as these processes most easily meet the criteria.

3.7 Characterization

There are a few analyses that can use to characterize the microstructure of the sample which are perform using Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), Fourier Transform Infrared Spectroscopy (FTIR), and Thermal Gravimetric Analysis (TGA). In this thesis, the characterizations of the catalyst were performing using SEM and FTIR.

3.7.1 Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) is a type of electron microscope that creates various images by focusing a high energy beam of electrons onto the surface of a sample and detecting signals from the interaction of the incident electrons with the sample's surface. The type of signals gathered in a SEM varies and can include secondary electrons, characteristic x-rays, and back scattered electrons. In SEM, these signals come not only from the primary beam impinging upon the sample, but from other interactions within the sample near the surface.

The SEM is capable of producing high-resolution images of a sample surface in its primary use mode, secondary electron imaging. Due to the manner in which this image is created, SEM images have great depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. This great depth of field and the wide range of magnifications are the most familiar imaging mode for specimens in the SEM. (Hergouth Lab).

3.7.2 Thermal Gravimetric Analysis (TGA)

Thermal Gravimetric Analysis (TGA) is simple analytical techniques that measure the weight loss or weight gain of a material as a function of temperature. As materials are heated, they can loose weight from a simple process such as drying, or from chemical reactions that liberate gasses. Some materials can gain weight by reacting with the atmosphere in the testing environment.

Since weight loss and gain are disruptive processes to the sample material or batch, knowledge of the magnitude and temperature range of those reactions are necessary in order to design adequate thermal ramps and holds during those critical reaction periods.

The method for example can be used to determine water of crystallization, follow degradation of materials, determine reaction kinetics, study oxidation and reduction, or to teach the principles of stoichiometry, formulae and analysis.

3.7.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantitative some components of an unknown mixture. It can be applied to the analysis of solids, liquids, and gasses. The term Fourier Transform Infrared Spectroscopy (FTIR) refers to a fairly recent development in the manner in which the data is collected and converted from an interference pattern to a spectrum.

FTIR can be used to identify chemicals from spills, paints, polymers, coatings, drugs, and contaminants. By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined. FTIR spectra of pure compounds are generally so unique that they are like a molecular "fingerprint". While organic compounds have very rich, detailed spectra, inorganic compounds are usually much simpler. For most common materials, the spectrum of an unknown can be identified by comparison to a library of known compounds.

Samples for FTIR can be prepared in a number of ways. For liquid samples, the easiest is to place one drop of sample between two plates of sodium chloride (salt). Salt is transparent to infrared light. The drop forms a thin film between the plates. Solid samples can be milled with potassium bromide (KBr) to form a very fine powder. This powder is then compressed into a thin pellet which can be analyzed. KBr is also transparent in the IR.

3.8 Catalyst deactivation

Catalyst life is an important property because it can control the economics of industrial processes. Catalysts can be deactivated by several factors such as poisoning and sintering. Catalyst poisons may sometimes be removed, depending on the nature of poison. However sintering is mainly irreversible so that it results in the need for catalyst replacement. In this section, deactivation by sintering and sulphur poisoning is reviewed.

3.8.1 Sintering

Sintering usually refers to the loss of active surface via structural modification of the catalyst. This is generally a thermally activated process and is physical in nature.

Sintering occurs both in supported metal catalysts and unsupported catalysts. In the former case, reduction of the active surface area is provoked via agglomeration and coalescence of small metal crystallites into larger ones with lower surface-to-volume ratios.

Two different but quite general pictures have been proposed for sintering of supported metal catalysts, i.e. the atomic migration and the crystallite migration models. In the first case, sintering occurs via escape of metal atoms from a crystallite, transport of these atoms across the surface of the support (or in the gas phase), and subsequent capture of the migrating atoms on collision with another metal crystallite.

Since larger crystallites are more stable (the metal-metal bond energies are often greater than the metal-support interaction), small crystallites diminish in size and the larger ones increase. The second model visualizes sintering to occur via migration of the crystallites along the surface of the support, followed by collision and coalescence of two crystallites.

As a matter of fact, sintering of supported metals involves complex physical and chemical phenomena that make the understanding of mechanistic aspects of the sintering a difficult task.

Experimental observations showed that sintering rates of supported metal catalysts are strongly affected by the temperature and to a lower extent by the atmosphere. The effect of temperature and atmosphere can be easily derived from constant temperature-variable time data such as those reported in Figure 3.3. The figure shows two different regimes a rapid, almost exponential loss of surface area during the initial stage and later on a slower (almost linear) loss. These data may be consistent with a shift from crystalline migration at low temperatures to atomic migration at high temperatures (Bartholomew, 1983).

Contrasting data are available concerning the effect of the atmosphere on sintering. For Pt-supported catalysts, several authors reported that under oxidizing atmosphere the sintering is more severe than under inert or reducing atmosphere. Bartholomew however observed that this is not a general case, since the rate of dispersion also depends on Pt loading (Figure 3.3) (Bartholomew, 1983).

These effects may be related to changes in surface structure due to adsorbed species such as H, O or OH in H_2, O_2 or H_2O-containing atmospheres, respectively. This points out the role of surface energy which depends on the gas composition and on the kinetics of the surface reactions.

Finally, the presence of strong metal-support interactions (SMSI) affect the spreading, wetting and redispersion of the supported metals: accordingly, because of the strong interaction of NiO with oxide supports, NiO/SiO_2 is thermally more stable in air than Ni/SiO_2 in H_2.(Bartholomew, 1994)

Along similar lines, Pd stabilizes Pt in O_2-containing atmospheres, possibly because of strong interactions of PdO with the oxide supports. Other factors affect the stability of a metal crystallite towards sintering, e.g. shape and size of the crystallite, support roughness and pore size impurities present in either the support or the metal.

Species such as carbon, oxygen, Ca, Ba, Ce or Ge may decrease metal atom mobility, while others such as Pb, Bi, Cl, F or S can increase the mobility. Rare earth oxides such as CeO_2 and La_2O_3 have been suggested to ``fix" noble metal atoms in automotive exhaust converters due to a strong, localized chemical interaction. (Bartholomew, 1983)

The effects of chlorides on the sintering of supported noble metal catalysts has been extensively investigated, since in several cases catalysts are prepared from chlorine-containing precursors (e.g. H_2PtCl_6) or are treated with chlorine-containing compounds to maintain or enhance their acid properties.

The presence of chlorine either in the gas-phase or on the support favors the sintering of Pt. However, recently there has been an accumulation of convincing experimental evidences that Cl favors a process opposite to sintering, i.e. redispersion. (Armor, 1985)

This process has been explained by either a physical splitting of the metal particles or to a spreading of metal monolayer over the surface. The redispersion is of industrial importance in catalytic reforming over $Pt/A_{l2}O_3$ catalysts, where it has been observed that appropriate chlorine treatments in the presence of oxygen during the catalyst regeneration procedures may be useful for Pt redispersion. This treatment, often termed as ``oxychlorination", possibly involves the transport of metal oxide or oxychloride molecules through the vapor or along the surface.

3.8.2 Sulphur poisoning

Natural gas may contain traces of sulphur and sulphur poisoning of catalysts has been extensively investigated. Sulphur exists in different chemical states depending on the reaction conditions. The adsorption of sulphur on most catalysts causes important modifications of the electronic and structural properties of the surface (Oudar, 1980).

Thus, the catalytic properties are also strongly affected. The presence of sulphur on the catalysts can either totally or partially inhibit the adsorption or the dissociation of molecular species and can also inhibit the surface reaction between adsorbed species.

During combustion, existing sulphur may react to produce sulphur dioxide, sulphur trioxide and sulphate species. It is well known that sulphur oxides can deactivate noble metal catalysts. The exception here is platinum, which is an excellent catalyst for the oxidation of sulphur dioxide (Taylor, 1976).

If the number of sulphate groups increased, the catalytic activity decreased and vice versa. It was also reported that these sulphate groups could be thermally destroyed either under vacuum or under nitrogen.

3.8.3 Other mechanisms of deactivation

Other mechanisms of deactivation include masking or pore blockage, caused e.g. by the physical deposit of substances on the outer surface of the catalyst thus hindering the active sites from reactants. In addition to the coke deposition already discussed, masking may occur during hydrotreating processes where metals (principally Ni and V) in the feedstock deposit on the catalyst external surface, or in the case of automotive exhaust converters by deposition of P (from lubricants) and Si compounds. (Oudar, 1980)

Certain catalysts may also suffer from loss of active phase. This may occur via processes like volatilization, e.g. Cu in the presence of Cl with formation of volatile $CuCl_2$, or Ru under oxidizing atmosphere at elevated temperatures via the formation of volatile RuOx, or formation of volatile carbonyls by reaction of metals with CO (Bartholomew, 1983).

Finally, loss of catalytic material due to attrition in moving or fluidized beds is a serious source of deactivation since the catalyst is continuously abraded away. Accordingly the availability of attrition-resistant catalysts for fluid-bed catalytic cracking is extremely important since the process operates with regeneration and catalyst recycles.

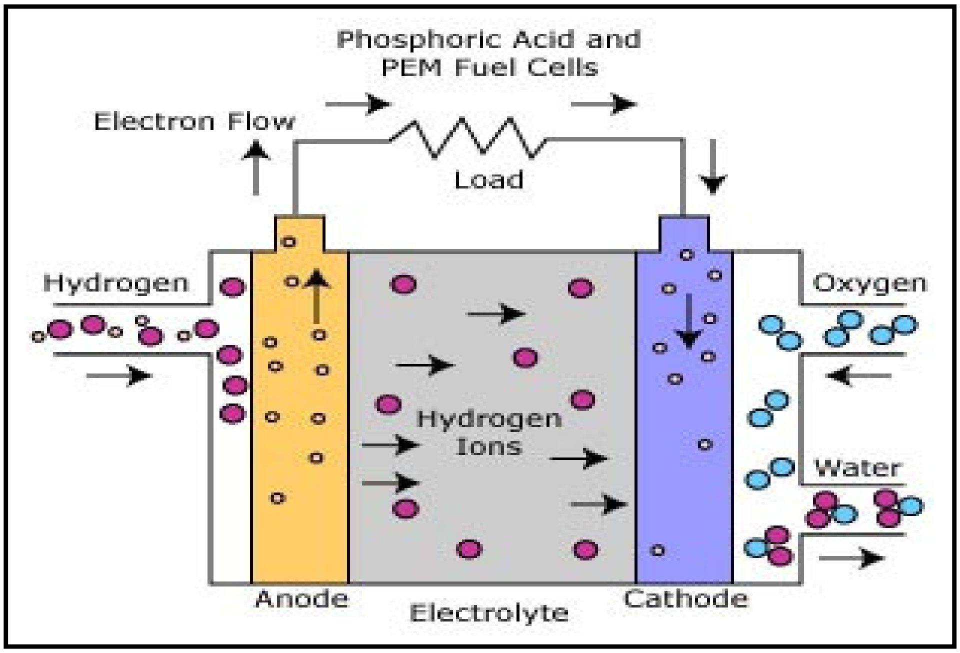

Figure 3.1: Proton Exchange Membrane Fuel Cell (PEMFC) stack operating Principle.

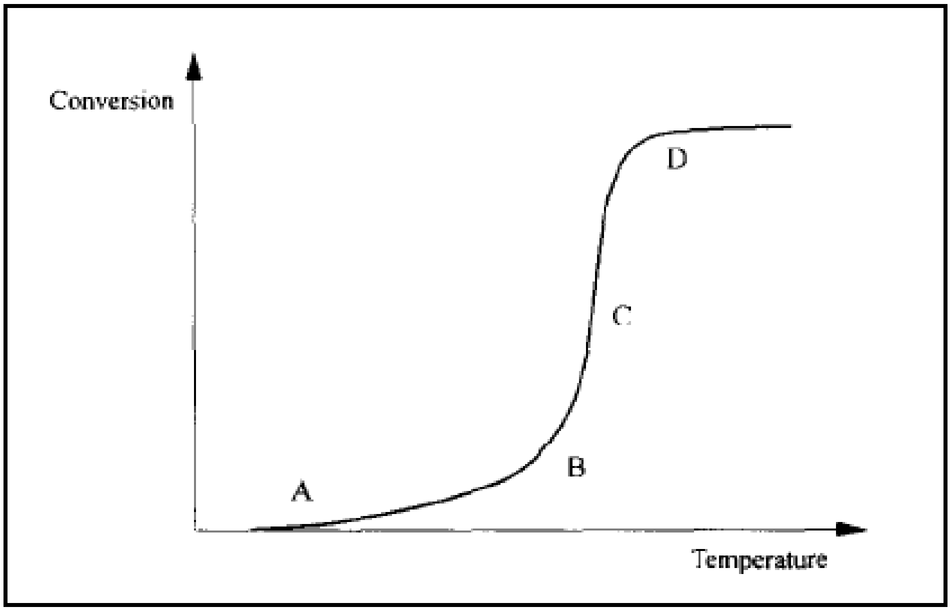

Figure 3.2: Conversion vs. temperature for catalytic combustion

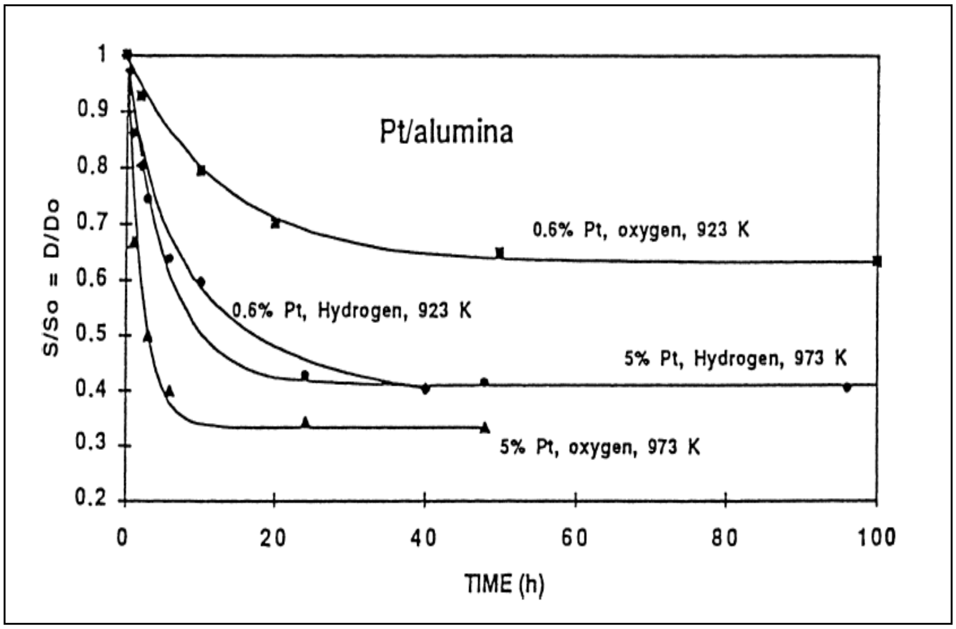

Figure 3.3: Effects of H_2 and O_2 atmospheres and of metal loading on sintering rates of Pt/Al_2O_3 catalysts (Bartholomew, 1983)

Table 3.1: Studies of the catalytic combustion of methane

Catalyst/support	Temp(^{0}C)	Air fuel ratio	Pretreatment of catalyst	CH4 Conversion
Co_3O_4	450	Air rich	-	-
0.5% Pd/Al_2O_3	450	Air rich	-	-
0.5% Pt/Al_2O_3	450	Air rich	-	-
Pd	290-480	2	Reduced with H_2 at 480^oC	5-80%
0.155%Pd/Al_2O_3	275-475	4	Heated to 500^oC in He	Up to 80%
0.153%Rh/Al_2O_3	350-500	4	containing 1% O_2	Up to 25%
0.22%Pt/Al_2O_3	300-500	4		Up to 10%
0.2% Pt/SiO_2	450	2	Reduced with H_2 at 300^oC	-
0.2%Pt/Al_2O_3	450	2		-
0.2%Pt/SiO2-Al_2O_3	450	2		-
2.7%Pt/γAl_2O_3	410	0.45		-
2.7%Pd/ γAl_2O_3	410	0.45		-
2.7%Pt/TiO_2	410	0.45	Heated to 500^oC in He or H_2	-
2.7%Pd/TiO_2	410	0.45		-
3.0%Pt/ThO_2	410	0.45		-
3.0%Pd/ThO_2	410	0.45		-
1.93%Pd/Al_2O_3 (i)	310-600	4	(i)Reduced with H_2 at 600^oC	-
1.93%Pd/Al_2O_3(ii)	310-600	4	(ii)preheated with O_2	-
Pd/ γAl_2O_3	289-432	1%CH4/ air	Calcined at 500^oC	-
Pd/SiO_2	290-422			-
1.95%Pt/Al_2O_3 (i)	280-600	4	(i)reduced with H_2 at 600^oC	-
1.95%Pt/Al_2O_3(ii)	280-600	4	(ii)preheated with O_2/CH_4 at 600^oC	-
0.16%Pd/Al_2O_3	250-700	5	Calcined with air at 500^oC	-
0.14%Rh/Al_2O_3	370-700	5		-
0.2%Pt/Al_2O_3	400-700	5		-

CHAPTER 4

METHODOLOGY

4.1 Research design

Mainly, this research can be separated into several sections which are catalyst preparation, catalyst characteristic and catalytic combustion. In first section, the research will focus on preparing Pt/Al_2O_3 catalyst from hexachloroplatinic acid by using impregnation method. Impregnation method is choosing because of the cheapest cost and the simplest among the other method.

Then entering the second section will start to observe the catalyst characterization by using scanning electron micrograph (SEM) and Fourier Transform Infrared spectroscopy (FTIR) to know the catalyst structure and platinum assisting inside the sample.

The last section is catalytic combustion of hydrogen in order to find the optimum temperature that can be reaching with different platinum loading of catalyst.

4.2 Material

4.2.1 Hexachloroplatinic acid

Hexachloroplatinic acid, purchased from Johnson matthey. It has a molecular weight 517.7 g/mol. It was an acidic solution with pH less the 1. The boiling point is 110^{o}C or 230^{o}F. Their Properties down to melting point 0^{o}C base on data for: water. It is easily soluble in cold water, hot water and diethyl ether. However, it was very toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment. (Merck MSDS, 2006)

4.2.2 Gaseous

Pure hydrogen and pure air used during catalyst performance testing. The purity of H_2 and air is 99.99% and >99% respectively. Gas was supplied from Malaysia Oxygen (MOX).

4.3 Catalyst preparation

The preparation procedure of alumina-supported platinum catalysts by impregnation method is shown in Figure 4.2. First Solution was prepared by dissolving the 39.6 grams of γ-Al_2O_3 Sigma-Aldrich with a grain size of 0.063–0.200 mm (70–230 mesh ASTM) into 200 grams distill water. A second solution was prepared by dissolving 1 gram of $H_2PtCl_6.xH_2O$ (Merck) into 10 grams of water and called as Pt salt solution.

This Pt salt solution was mixed with the alumina solution at 20^{o}C and the mixture (slurry) was vigorously stirred for 2 h as show in figure 4.2. The color of the slurry was observed and it’s become pale yellow and heterogeneous solution because the alumina was not dissolved in water. The slurry was keep stirred at rotation 500 ramp per minute.

The surface of the alumina participates in the reduction of the metal of catalyzes the reduction, so that the reduction occur on, and only on, the surface of the alumina.(William,1998) This leads to high dispersion of the catalyst metal on the alumina, which in turn generates high catalytic activity.

In this case, a solution of $H_2PtCl_6.xH_2O$ was used that contains the theoretical amount of hydrazine needed to reduce the platinum from chloride according to this following reaction:

$$H_2PtCl_6 + NH_2NH_2 \quad \rightarrow \quad Pt + N_2 + 6HCl \qquad (4.1)$$

The Hydrazine was added in droplet with very small amount. The reduction is indicated by the color of the slurry, which changes from pale yellow to black or gray as show in Figure 4.3. The reaction of hexachloroplatinic acid with Hydrazine will produce of Hydrochloric Acid. The pH of the solution was measured and the value is pH 1. So the pH of solution need to adjusted until pH 4. (Trimm, 1999)

Some of 1M of Sodium Hydroxide (NaOH) is added until the pH value reach 4, followed by Impregnation process for 2 weeks. The biker of the slurry was covered by aluminium soil to avoid light promoted. (Taylor, 1999)

The water solvent was removed by drying at temperature 100^oC for 2 hour. A rigid solid was formed after the solvent removal. The resulting solid was dried at 120^oC for 3 hour in an oven, followed by calcination under air flow in a crucible. The airflow rate was $2Lmin^{-1}g^{-1}$.The temperature was linearly increased from room temperature to 550^oC over 3 h and then maintained at 550^oC for 6 hour.

After complete calcination process, the solid was crushed to form powder. In order to get the uniform size, the solid was sieve at size 300 μm. The sample was dividing to two for characteristic analyzing and catalytic combustion.

4.4 Catalyst characterization

4.4.1 Scanning electron Micrograph (SEM)

The scanning electron micrograph (SEM) is a type of electron microscope capable of producing high resolution images of a sample surface. Due to the manner in which the image is created, SEM images have a characteristic three-dimensional appearance and are useful for judging the morphology of the structure and porous structure of the sample. In this experiment the type of SEM used is ZEISS EVO 50.

Powder specimens require no special preparation for SEM, except for trimming to appropriate size to fit in a specimen chamber, and make appropriate sectioning if necessary. A finely focused electron beam scanned across the surface of the sample generates secondary electrons, backscattered electrons, and characteristic X-rays. These signals are collected by detectors to form images of the sample displayed on a cathode ray tube screen.

Features seen in the SEM image may then be immediately analyzed for elemental composition using EDS or WDS. Secondary Electron Imaging shows the topography of surface features a few nm across. Films and stains as thin as 20 nm produce adequate-contrast images. Samples are viewed at useful magnifications up to 100 000x without the need for extensive sample preparation and without damaging the sample. Even higher magnifications and resolution are routinely obtained from Field Emission SEM. Data Output is generated in real time on the CRT monitor.

4.4.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantitative some components of an unknown mixture. It can be applied to the analysis of solids, liquids, and gasses. The term Fourier Transform Infrared Spectroscopy (FTIR) refers to a fairly recent development in the manner in which the data is collected and converted from an interference pattern to a spectrum. FTIR is perhaps the most powerful tool for identifying types of chemical bonds (functional groups). The wavelength of light absorbed is characteristic of the chemical bond as can be seen in this annotated spectrum.

Source generates light across the spectrum of interest. A monochromater (in IR this can be either a salt prism or a grating with finely spaced etched lines) separates the source radiation into its different wavelengths. A slit selects the collection of wavelengths that shine through the sample at any given time. In double beam operation, a beam splitter separates the incident beam in two; half goes to the sample, and half to a reference.

The sample absorbs light according to its chemical properties. A detector collects the radiation that passes through the sample, and in double-beam operation, compares its energy to that going through the reference. The detector puts out an electrical signal, which is normally sent directly to an analog recorder. A link between the monochromater and the recorder allows to record energy as a function of frequency or wavelength, depending on how the recorder is calibrated.

4.5 Performance Testing

The catalyst was tested by running a hydrogen catalytic combustion. The catalyst was weighted at 0.06 gram and added into glass reactor. The reactor was preparing first by adding a glass wool as a support for the catalyst as shown in figure 4.6

Before the catalytic combustion started, the catalyst need to make a reduction by using hydrogen gas. It is because the Platinum inside the catalyst is a platinum oxide (PtO_2). In order to perform a higher activity of catalyst, the PtO_2 need to reduce to get a pure Pt.

The catalyst was heated until 350°C with ramping temperature at 3°C per minutes by using electrical furnace. After the catalyst was heated, hydrogen gas was flowed through the catalyst for two hours. The reaction of reduction process as followed:

$$PtO_2 + H_2 \rightarrow Pt + H_2O \tag{4.2}$$

After two hours, the catalyst was cooled naturally until ambient temperature. The hydrogen gas was stopped and replaced by nitrogen gas. Nitrogen gas was keep flow until the testing was run.

The testing was set hydrogen to air ratio at 46%. The temperature of catalyst was measured by using thermocouple that install close with catalyst surface. The increasing of the catalyst temperature was observed.

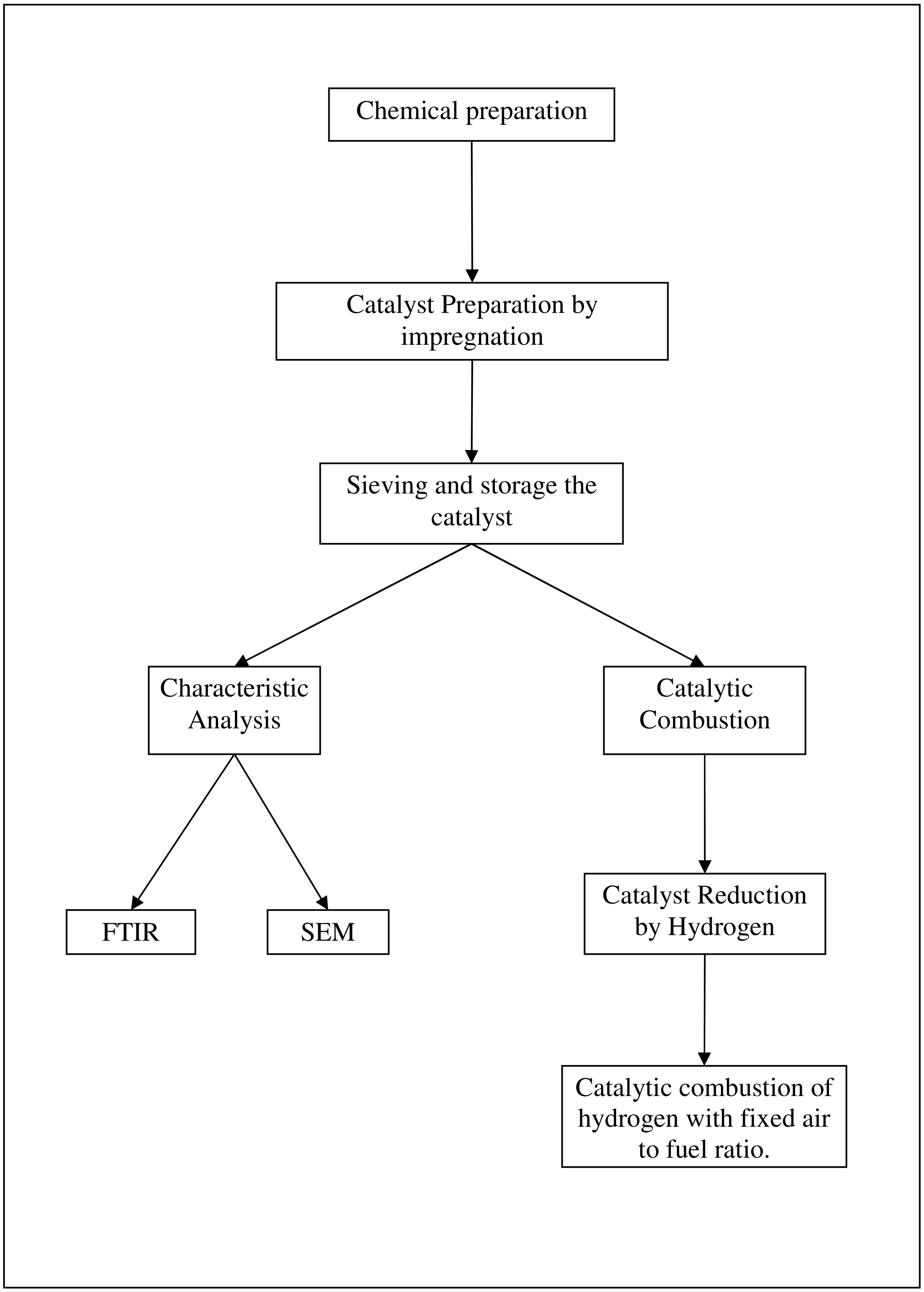

Figure 4.1: Overall Methodology

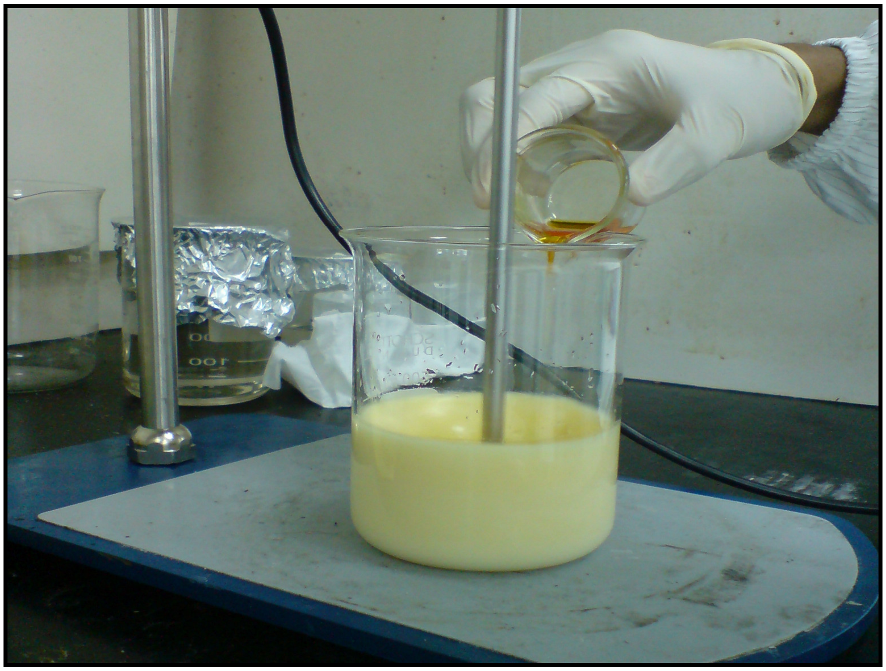

Figure 4.2: The mixture of hexachloroplatinic acid and alumina form a pale yellow solution

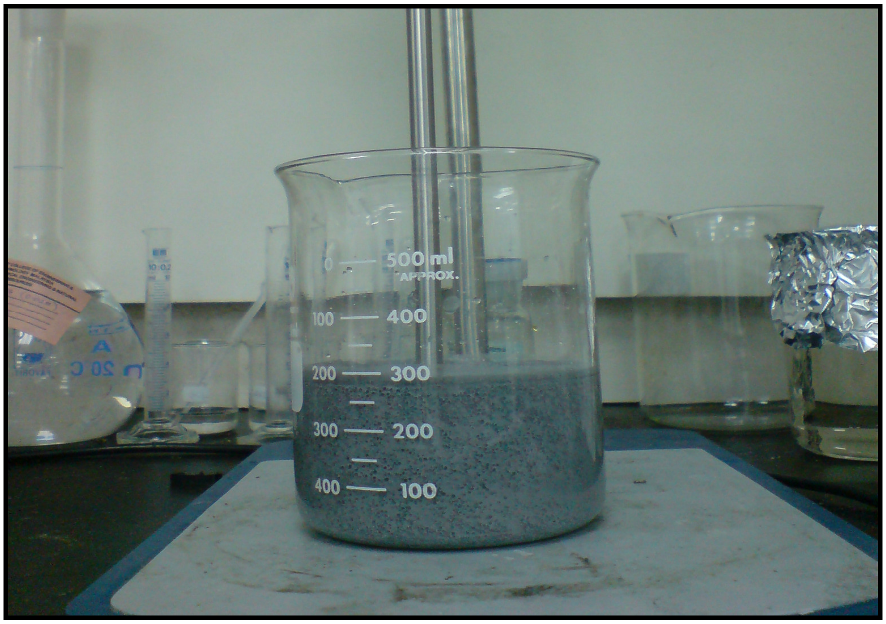

Figure 4.3: The color of solution (slurry) was change to gray after additional of hydrazine.

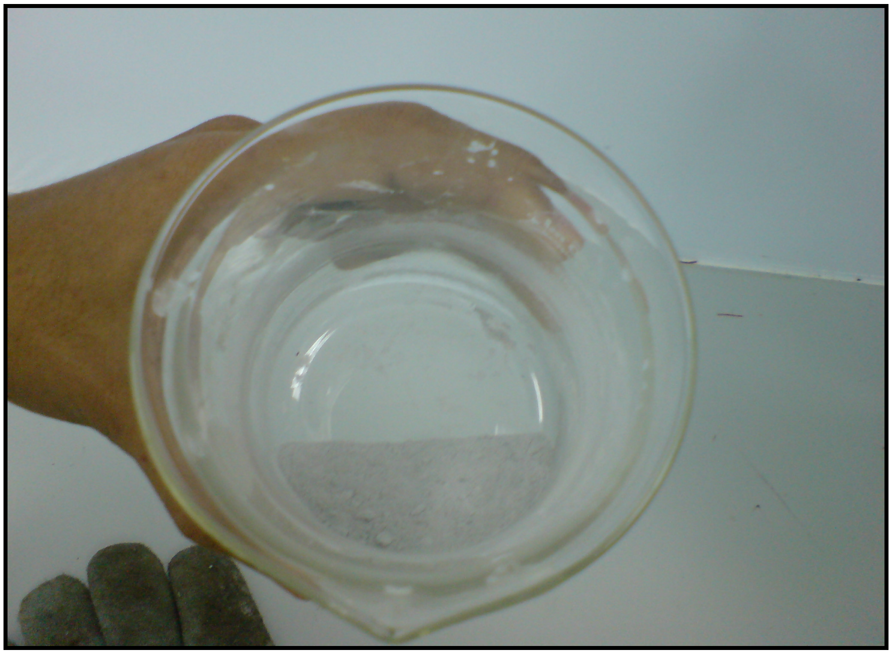

Figure 4.4: Picture of Platinum and Alumina mixture after the drying process.

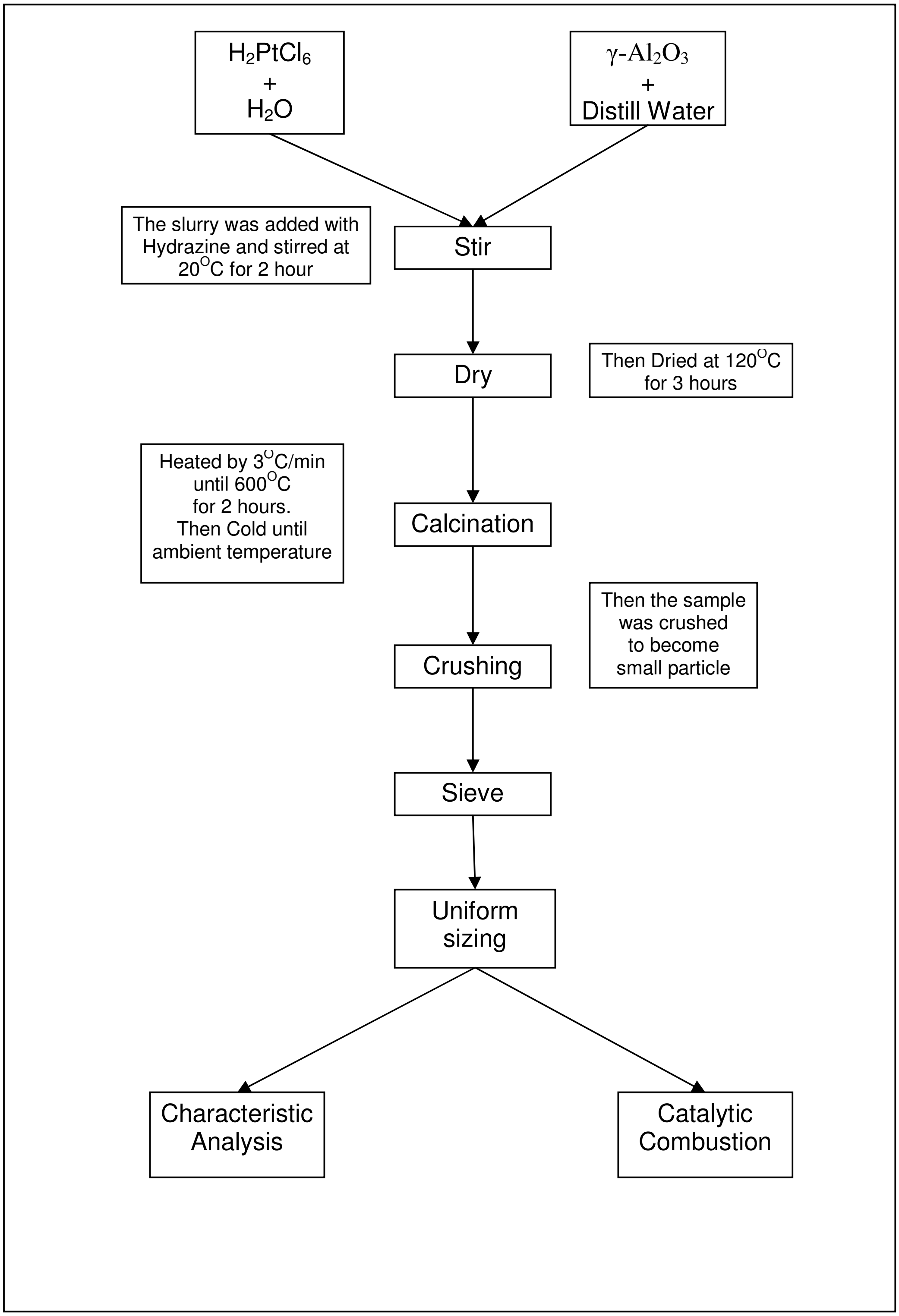

Figure 4.5: Summary of the catalyst preparation process.

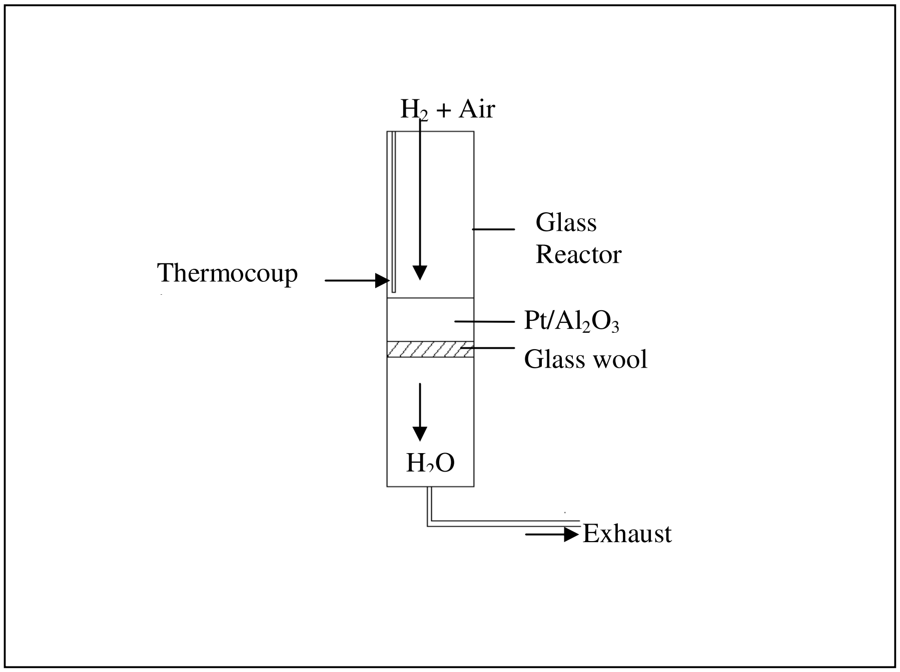

Figure 4.6: Schematic diagram of the Pt/Al_2O_3 catalyst position in the glass reactor

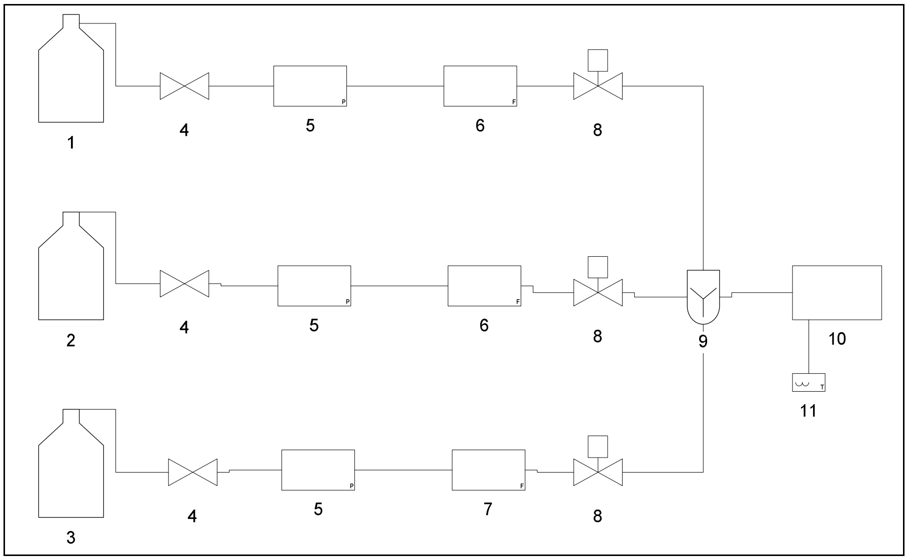

Figure 4.7: Schematic diagram of the catalytic combustion rig. 1.Purified air; 2.Hydrogen cylinder; 3.Nitrogen cylinder; 4.Valve; 5.Pressure gauge; 6.Scientific mass flow meter; 7.Volumetric flow meter; 8.Check valve; 9.Static mixing chamber; 10.Electrical furnace; 11.Thermocouple probes.

CHAPTER 5

RESULT AND DISCUSSION

5.1 Catalyst Preparation

The preparation process was follow according to the methodology in Chapter 3. Base on past journal, there are a lot of condition during preparing the catalyst as summarized in Table 2.2. Additional of Hydrazine is some modification from the basic impregnation method. Hydrazine is an agent to reduce ion chloride from platinum to get pure platinum inside the catalyst.

The effects of chlorides on the sintering of supported noble metal catalysts has been extensively investigated, since in several cases catalysts are prepared from chlorine-containing precursors (e.g. H_2PtCl_6) or are treated with chlorine-containing compounds to maintain or enhance their acid properties. The presence of chlorine either in the gas-phase or on the support favors the sintering of Pt. (Wanke, 1975)

The hydrazine added by droplet into slurry during preparation. The pH of solution measured and the result is about pH1. It is found that the present of Hydrochloric acid (HCl) was affecting the pH value. The best pH for this solution is 4. (Trimm, 1991)

In order to increase the pH value to pH4, some of 1M Sodium hydroxide (NaOH) was added into solution. After added an amount of NaOH, the pH value was does not change. The result will affect the catalyst activity because the pH value of solution was not at pH4.

5.2 Catalyst Characteristic

5.2.1 Porous Structure of Support

For catalytic combustion, special metal alloys or ceramics are usually used for fabrication of substrates, depending on the required operating temperature. Metal alloys, which are made of iron, chrome and aluminium, provide excellent mechanical properties and a thinner cell wall, but their thermal stability is not as high as ceramics.

Therefore, ceramics have been used far more than metal alloys in the past. The most common high temperature ceramics are based on alumina which is relatively inexpensive and reasonably resistant to thermal shock.

Alumina is mainly used for catalytic combustors in order to obtain high geometric areas of the catalyst and low pressure drop through the system. The choice of alumina material is because of physical and chemical properties such as surface area, porosity, thermal stability, thermal conductivity, reactivity with reactants or products, chemical stability and catalytic activity.

For catalytic combustion, a high surface area is required to disperse the platinum. The most commonly used material is γ-$A1_20_3$, the surface area of which is quite high. Figure 5.1 shows SEM micrographs of alumina after calcine at 550^0C. This figure shows the porous structure of alumina at 300 X magnification. This high porous structure will allowed a large amount of oxygen can absorbed into the catalyst.

5.2.2 Platinum dispersion

It was observed that hydrogen oxidation over platinum was a structure-sensitive reaction. Hicks (Hicks, 1990) explained that this structure sensitivity was caused by the different reactivities of adsorbed oxygen on the surfaces of platinum.

For platinum, two types of platinum particles on the support exist. One is completely dispersed platinum and the other is in the form of crystallites of platinum. (Trimm, 1990) Figure 5.2 show the crystallites structure inside the catalyst. It is can identify as platinum.

In the former case, platinum is oxidized to PtO_2 whereas, in the latter system, oxygen is adsorbed on the crystallites to provide highly reactive adsorbed oxygen. The crystallites of platinum (large particles) are therefore more active than dispersed platinum (small particles). (Trimm, 1990)

The structures of Pt/Al_2O_3 viewed by using the Scanning Electron Microscopy (SEM) at 1000 X magnification. The size of crystallites platinum is approximately 20µm. The other type of platinum particle which is dispersed platinum is a nano-size particle. (Christos, 2007)

The limitation of (SEM) equipment is only at micro magnification. Equipment such as Transmission Electron Microscopy (TEM) can be able to view until nano magnification. Figure 5.3 show the TEM scanning result with 100,000 magnifications.

Figure 5.4 show the FTIR result of 1 %wt Pt/Al_2O_3 which is representing as red line and 3% wt Pt/Al_2O_3 as a blue line. From the FTIR profile, it shows main peak maximum of 728 cm^{-1} until 699 cm^{-1}. This peak can be related to the presented of Platinum in the alumina support. (Fuks, 2005)

According to Fuks, the peak with maximum wave length is not totally presented as pure platinum. The wave length 728cm^{-1} until 699 cm^{-1} can be consist of PtO_2, $PtCl_6$ and Pt it self. From figure 5.4, there are three highest peaks that can identify as a group of platinum.

5.3 Catalyst Testing

5.3.1 Pretreatment

The effect of Pt loading on the support on the oxidation of hydrogen was investigated. 1wt% and 3wt% Pt loading over alumina supported was tested at same condition. The objective of this catalytic combustion is to look the effect of different platinum weight loading inside the catalyst. Any other parameter that will affect the result was fixed. Before performing catalytic combustion, the catalyst needs to treat.

The activity of the catalyst was found to be significantly dependent on gases used for catalyst pretreatment. The effect of pretreatment on the activity of Pt and Pd catalysts was studied with H_2, He and O_2. Pretreatment with H_2 increased the activity of catalysts whereas O_2 decreased the activity. Reactant gases were also used for the pretreatment of catalysts. (Otto, 1989)

In this testing, Hydrogen gas was used for catalyst pretreatment. Base on SEM result, the active metal that consists in the catalyst is PtO_2. The hydrogen gas will react with ion oxide to form H_2O as shown in equation 4.2. The active metal was change the platinum to form Pt/Al_2O_3. So it will increase the activity of catalyst.

5.3.2 Testing Result

The catalyst weight used in this combustion is 0.06 grams for both samples. Hydrogen to air ration was setting at 46% with pressure at 1 bar. These two parameters were fixed to avoid any affect to the result.

Figure 5.5 show the result of catalytic combustion over hydrogen with 1wt% and 3wt% of Pt weight loading catalyst. For 1wt% Pt/Al_2O_3 catalyst, the ignition temperature was occurred at ambient temperature which is at 27^oC. The temperature rise rapidly in one minute and reach at 278^oC. For the second minutes, the temperature maintains at 278^{o}C and start decrease at third minutes. After four minutes, the testing was stop because of temperature decrease.

For 3wt% Pt/Al_2O_3 catalyst, the ignition temperature was occurred at 27^{o}C. The temperature rise rapidly and reach at 328^{o}C in one minutes. After two minutes, the temperature rise again to reach at 362^{o}C. The temperature was maintained and same temperature until fifth minutes and testing was stopped.

Base of temperature profile of 1wt% Pt/Al_2O_3 catalyst, the decreasing after second minutes was investigated. It was affected by Oxygen adsorption is much faster then there of hydrogen and oxygen species cover the surface despite the lower oxygen concentration in the gas phased. Hydrogen molecules, which dissociate on the catalyst, are completely oxidized to H_2O, such that only complete oxidation products are observed in the mixture. (Wanke, 1975)

However, the temperature profile for 3wt% Pt/Al_2O_3, It show the increasing curved that reach at temperature 362^{o}C. With natural gas, it is somewhat easier to control temperature, since the presence of overall amounts of higher hydrocarbons allows initiation of oxidation at lower temperatures. The light-off temperature of methane at an air: fuel ratio of 46% is 360°C (Trimm 1990). It proved that the catalyst with 3wt% of Pt/Al_2O_3 can heat the Autothermal Reformer (ATR) until 362^{o}C.

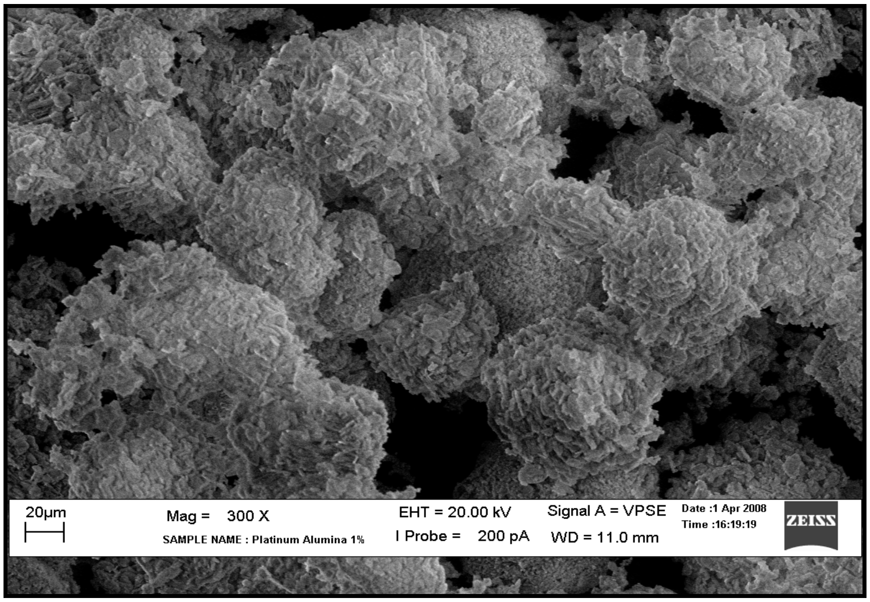

Figure 5.1: SEM micrograph of the platinum-alumina illustrated area. The porous structure diameter is approximately 40µm.

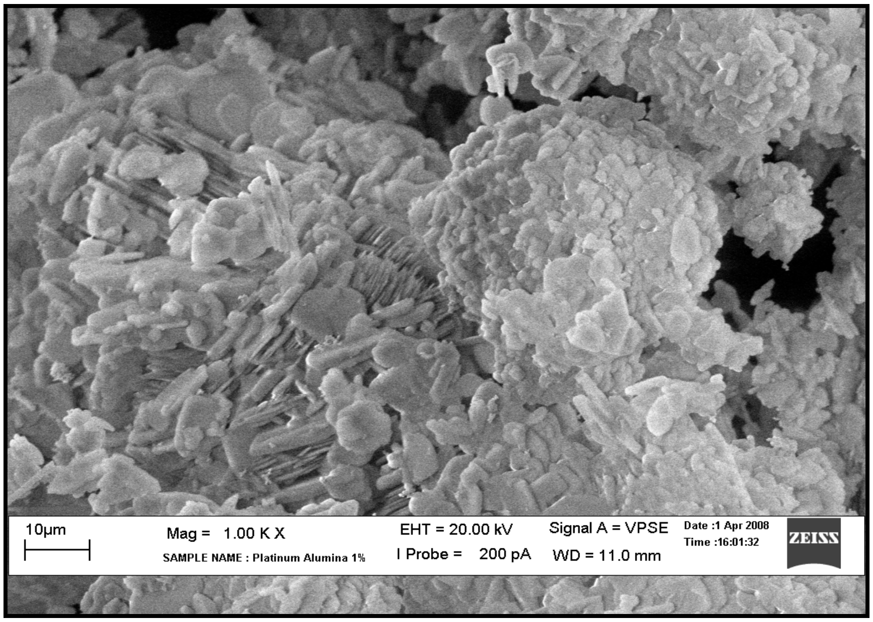

Figure 5.2: Crystallites structure was observed in Pt/Al_2O_3 by scanning electron microscopy (SEM).

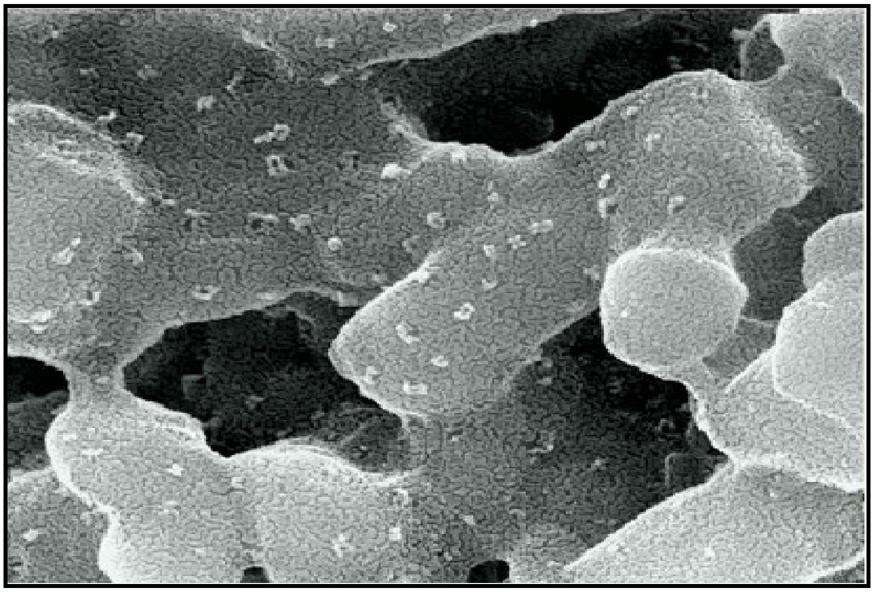

Figure 5.3: Platinum particle are completely disperse on alumina surface. White dot represent platinum particle. (Christos, 2007)

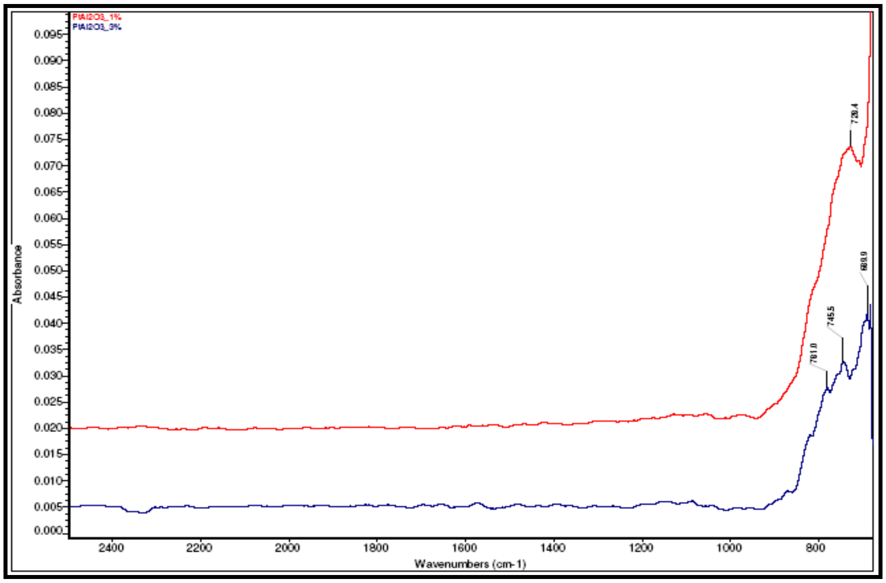

Figure 5.4: Result of FTIR spectrometer on platinum alumina. Red line represent 1% wt Platinum and Blue line represent 3% wt Platinum.

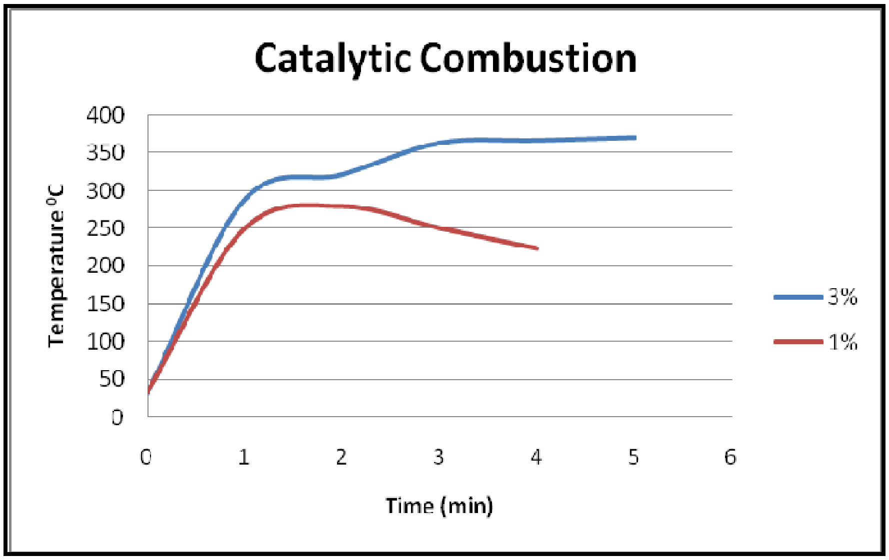

Figure 5.5: Result of catalytic combustion of hydrogen over different platinum weight loading

CHAPTER 6

CONCLUSION & RECOMMENDATION

6.1 Preparation method of Pt/Al_2O_3 Catalyst

The preparation of catalyst by impregnation method was run with a condition established by pass research. Some modification from regular impregnation method was done by additional of hydrazine. Hydrazine is an agent to reduce ion chloride from platinum.

During preparation, the pH value does not give big effect to the result of sample. Base on experiment, even the pH value of the solution is 1, the platinum still can dispersed onto alumina.

The characteristic that have investigated for the sample is using SEM and FTIR. The characteristic investigation shows that the platinum dispersed well onto alumina. The image result from SEM shows the porous structure of the alumina support. At 1000 magnification image show the crystal structure that can be identify as platinum.

From FTIR result, the main peak with maximum at 728cm^{-1} until 699cm^{-1} can be related to the presented of platinum in the alumina. According to pass research tell that the platinum in the catalyst can be consisting of PtO2, PtCl and Pt itself.

6.2 The Optimum Temperature by Catalytic Combustion of Hydrogen

After catalyst characterization, the catalyst was testing by catalytic combustion of hydrogen with fixed air to fuel ration condition. Before the catalytic combustion can be perform, the catalyst need to reduce by using Hydrogen gas to increase the catalyst activity.

The result show that the combustion occurred at ambient temperature which is at $27^{o}C$. The different Platinum weight loading catalyst show a different temperature profile where the higher Platinum weight loading show the temperature increase faster and higher compare to lower Platinum loading catalyst.

Base on combustion result, 3 wt% Pt/Al_2O_3 was achieve a target temperature at $362^{0}C$ which temperature needed by ATR to reform the methane to hydrogen.

6.3 Recommendations

Although, at the end of this study, preheating system was determined as the potential routes for supply heat to autothermal reformer catalyst, a series of extended works must be incessantly done to make it more competently feasible. Hence, the future work in this field would focus on the following subjects:

i) The Future study should also concentrate on another method for preparation of Pt/Al_2O_3 catalyst. There are a lot of new invention methods to dispersed platinum onto alumina support. Impregnation method has an advantage as a cheapest method. However, this method is suitable for small scale production of catalyst. The selection preparation method should be suitable with chemical that will be used in preparation.

ii) The preparation of Pt/Al_2O_3 was perform with different weight loading which is 1wt% and 3wt% from hexachloroplatinic acid

(H_2PtCl_6) by using impregnation method. Base on the pass research, 5 wt% Pt/Al_2O_3 catalyst will increase the temperature higher and faster during catalytic combustion of hydrogen. Suggestion was focused on Platinum weight loading selection. In order to get clearly different temperature profile, the platinum weight loading should be choose from 1 wt% to 10wt%. But it is of cause will affect the cost of the research.

iii) Additional a Hydrazine into slurry solution during preparation is to reduce ion chloride from platinum. However, the reaction will produce another component which is Hydrochloric Acid (HCl). The result will change the pH value to the solution become more acidic. The best pH value for preparing solution is about 4. Event it not gives a big effect to the result, but every consideration will give higher activity to the catalyst performance.

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APPENDIX A

Calculation of Platinum Weight Loading

A.1 Calculation on Platinum contain in 1 gram H_2PtCl_6.

Molecular weight

for

H_2PtCl_6 x $6H_2O$ = 2(1) + 195 + 6(35.45) + 6(18)

= 517.7 g/mol

γ-Al_2O_3 = 2(27) + 3(16)

= 102 g/mol

Purity (H_2PtCl_6) = 99.9%

So, 517.7 g/mol x 0.999 = 517 g/mol

To find the Pt over H_2PtCl_6 ratio,

$$\frac{195\ \text{g/mol Pt}}{415\ \text{g/mol } H_2PtCl_6} = 0.47$$

Assume,

10 mg H_2PtCl_6 x $6H_2O$= 4.7 mg Pt

And 1 g Al_2O_3

Total Weight = 1.0047 g

Pt loading $= \dfrac{0.0047\ \text{g Pt}}{1.0047\ \text{g Pt}/Al_2O_3}$

= **0.47 wt% Pt/Al_2O_3**

A.2 Calculation on preparation of 50 grams 1wt% Pt/Al_2O_3

$$\text{Pt loading} \quad 1\text{wt\%} = \frac{X \text{ g Pt}}{50 \text{ g } Pt/Al_2O_3}$$

$$= 0.5 \text{ g Pt}$$

Amount of H_2PtCl_6:

$$\frac{0.5 \text{ g Pt}}{X \text{ g } H_2PtCl_6} = 0.40$$

$$= 1.25 \text{ g } H_2PtCl_6$$

A.3 Calculation on preparation of 50 grams 3wt% Pt/Al_2O_3

$$\text{Pt loading} \quad 3\text{wt\%} = \frac{X \text{ g Pt}}{50 \text{ g } Pt/Al_2O_3}$$

$$= 1.5 \text{ g Pt}$$

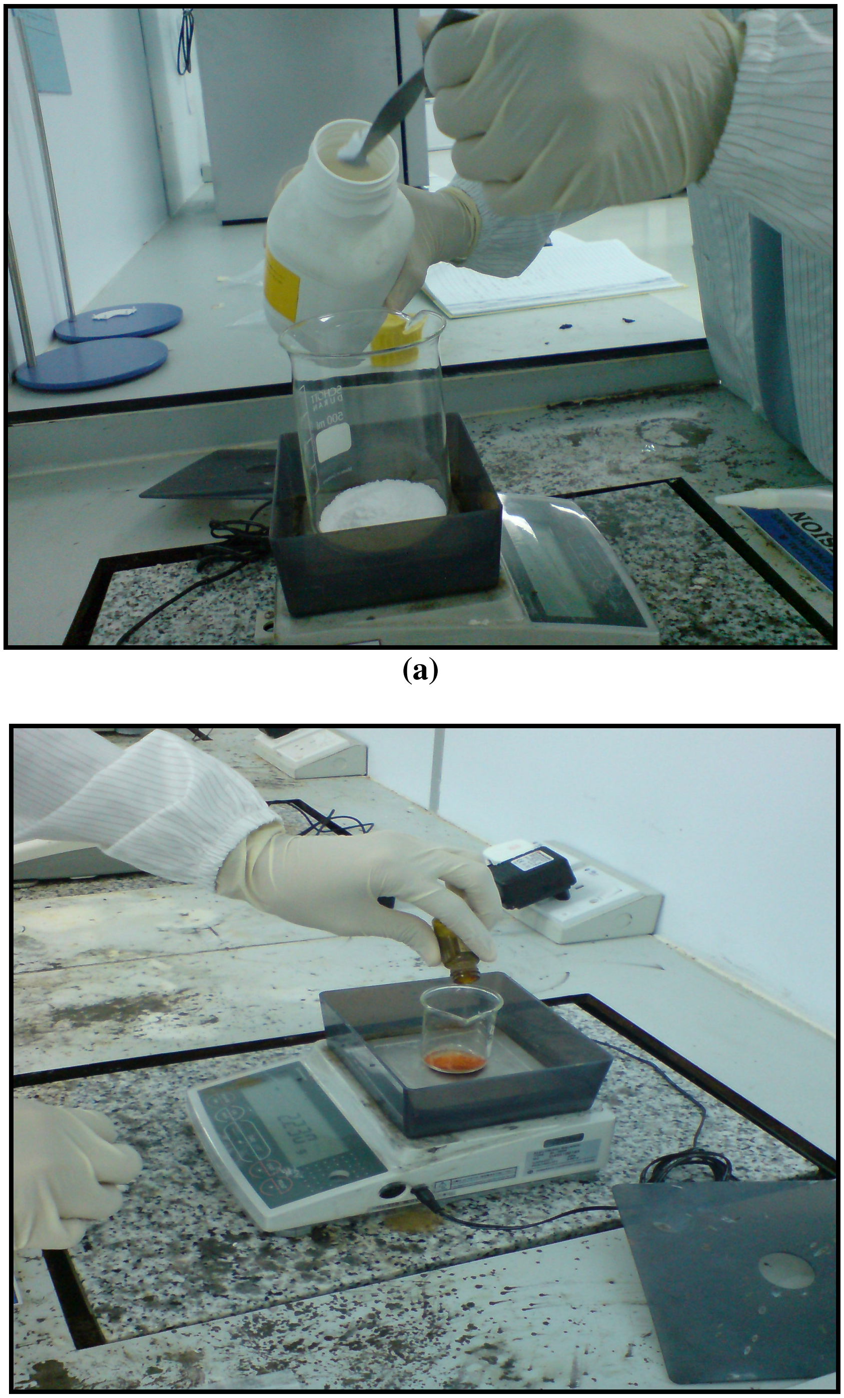
Amount of H_2PtCl_6:

$$\frac{1.5 \text{ g Pt}}{X \text{ g } H_2PtCl_6} = 0.40$$

$$= 3.75 \text{ g } H_2PtCl_6$$

APPENDIX B

Preparation of Platinum Alumina (Pt/Al_2O_3) and Catalyst Testing



(a)

(b)

Figure B.1: Preparation of (a) Alumina and (b) hexachloroplatinic acid before mixed with distil water.

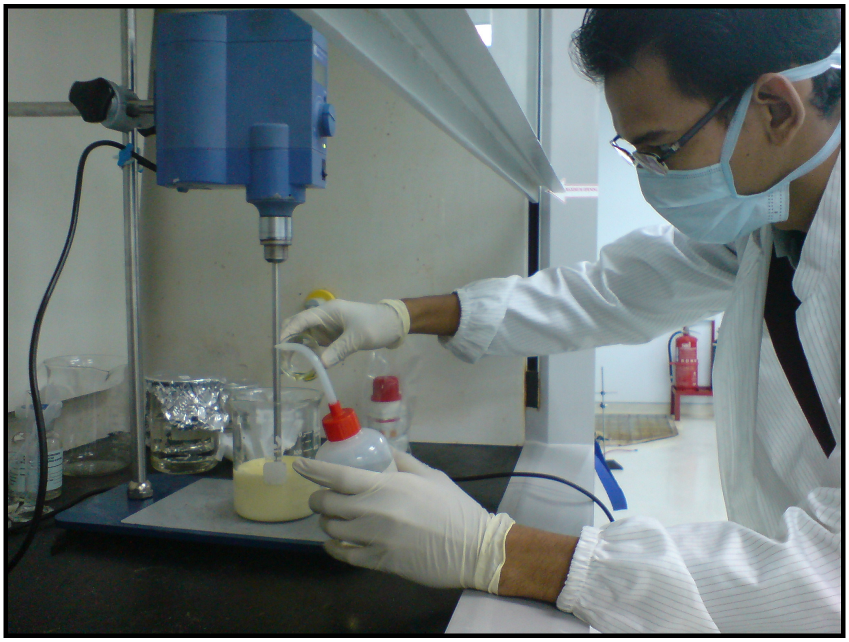


Figure B.2: Mixing process of Alumina solution and Hexachloroplatinic Acid and form pale yellow solution

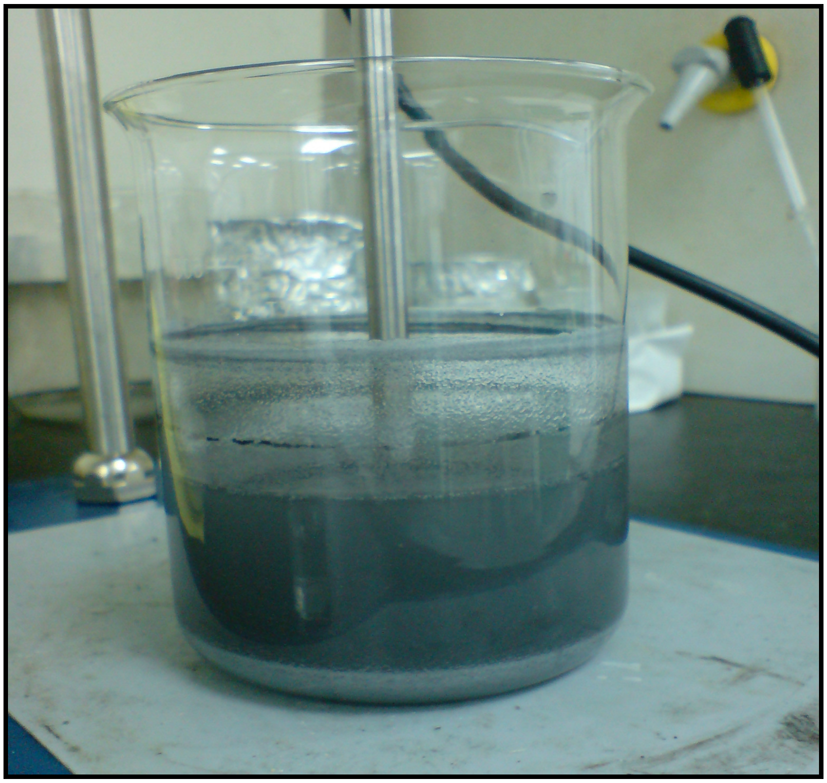


Figure B.3: Picture of slurry after addition of hydrazine and stirred for 2 h.

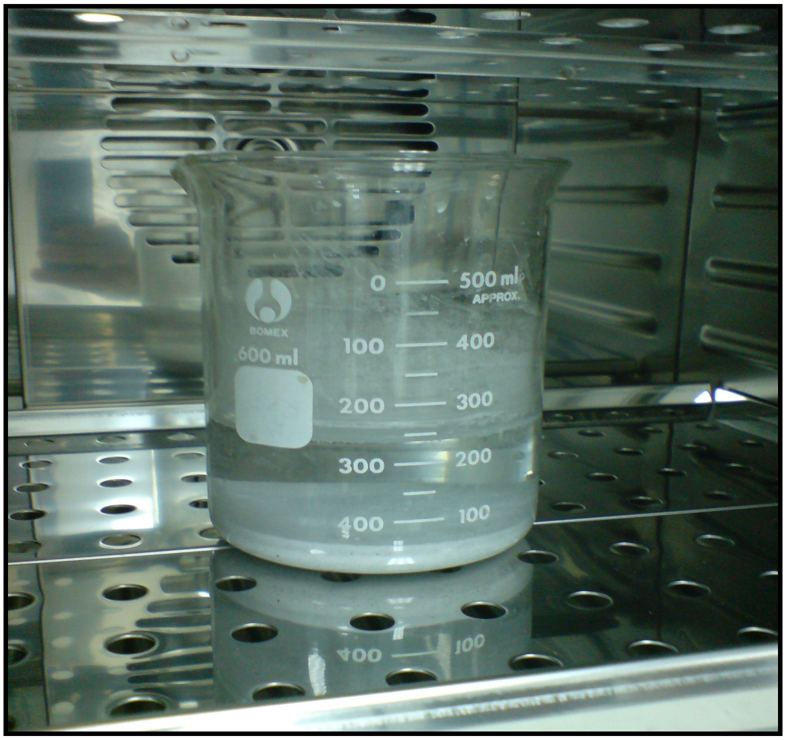


Figure B.4: Picture of drying process after the sample was impregnate for 2 weeks.

Figure B.5: Picture of sample after drying in oven at 120°C for over night.

Figure B.6: Picture of Rig that used to run catalytic combustion

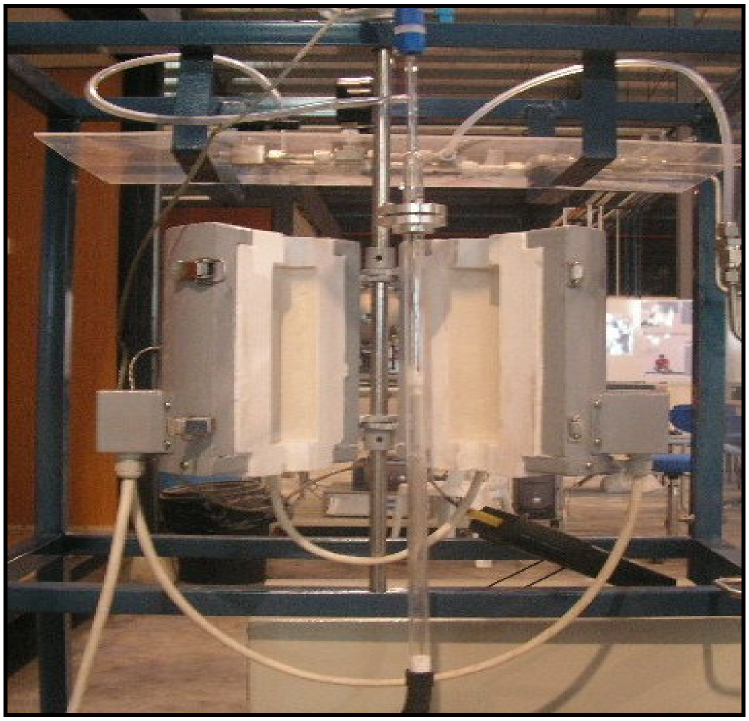


Figure B.7: Picture of electrical furnace that used for catalyst treatment.

APPENDIX C

Material Safety Data Sheet (MSDS)