CHAPTER III
EXPERIMENTAL

This chapter will initially provide information of materials used in the experiment. Individual catalyst preparation technique and the experimental equipment along with testing procedures are explained in the following section. Analytical instrumentation applied as a tool to determine inlet and outlet gas streams both qualitatively and quantitatively is illustrated as well. Last section will describe basic theory and instrumental detail of the characterization techniques that were employed for studying the properties of the catalysts.

3.1 Materials

3.1.1 Chemicals

All chemicals used in this work were analytical grade. Their purity and manufacturer are shown in Table 3.1. In addition, deionized water was used in catalyst preparation and for humidifying gas stream in catalytic activity test.

3.1.2 Gases

Reactant gases and calibration gases including GC reference and carrier gases are listed as follows:

- Nitric oxide (NO) 5% and 0.95% in helium were obtained from Air Products and Chemicals and Cryogenic Gas Inc., respectively.
- Propene (C_3H_6) 0.91% and 1% in helium were obtained from Thai Industrial Gas (Public) Co., Ltd. and Cryogenic Gas Inc., respectively.
- Ammonia (NH_3) 1.052% in helium was obtained from Cryogenic Gas Inc.
- Sulfur dioxide (SO_2) 306 ppm in helium was obtained from Cryogenic Gas Inc.
- Ultra high purity (UHP) oxygen (O_2) was obtained from Praxair (Thailand) Co., Ltd. and Cryogenic Gas Inc.

- Ultra high purity (UHP) helium (He) was obtained from Thai Industrial Gas (Public) Co., Ltd. and Cryogenic Gas Inc.
- Nitrogen (N_2) 3.11% in helium used as a standard gas was obtained from Thai Industrial Gas (Public) Co., Ltd.

3.2 Catalyst Preparation

The different preparation techniques and heat treatment were carried out in order to compare the activity of the catalysts as follows:

3.2.1 Single Step Sol-gel

In general, sol-gel synthesis has several promising advantages because it offers high purity, homogeneity, and availability to control the composition, the texture and structural properties such as surface area, pore size distribution, and porosity. Four main steps are executed in sol-gel preparation: a hydrogel formation, aging, solvent removal, and heat treatment (Ertl *et al.*, 1997). The process first involves sol formation followed by gel formation. A precursor in preparation can be either metal salt or metal alkoxide. However, metal alkoxides have been extensively used due to their commercial availability in high purity and their well-known solution chemistry.

Two types of aluminum alkoxide were used as an initial chemical in this sol-gel synthesis to form alumina support. Pt and Au were active ingredients of the finished catalysts. A precursor of the active metal was introduced during the sol state so called single step sol-gel method. Hydrogen hexachlorideplatinate (IV) hydrate and gold (III) acetate were metal precursors used in the preparation of Pt and Au catalysts, respectively. The details of the catalyst preparation from each precursor are given as the followings:

Table 3.1 The manufacturer and purity of the chemicals

Chemical	Manufacturer	Purity (%)
Hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4.3H_2O$)	Aldrich	≥ 99.9 (traces metals basis)
Gold (III) acetate ($Au(O_2CCH_3)_3$)	Alfa Aesar	99.9 (metals basis)
Dihydrogen hexachloroplatinate (IV) hydrate ($H_2PtCl_6.xH_2O$)	A Johnson Matthey Company	99.999 (metals basis)
Aluminum isopropoxide ($Al[OCH(CH_3)_2]_3$)	Alfa Aesar	≥ 99.99 (metals basis)
Aluminum tri-*sec*-butoxide ($Al[O(CH_3)CHC_2H_5]_3$)	Alfa Aesar	95
Aluminum oxide, activated, neutral, gamma-phase (γ-Al_2O_3)	Aldrich	surface area: 150 m^2/g pore size: 58 Å
Ethanol (CH_3CH_2OH)	Aldrich	≥ 99.5 (anhydrous)
Isopropanol ($(CH_3)_2CHOH$)	Aldrich	99.5 (anhydrous)
1,3-Butanediol ($CH_3CH(OH)CH_2CH_2OH$)	Aldrich	≥ 99 (anhydrous)
Ethylenediamine ($NH_2CH_2CH_2NH_2$)	Fluka	≥ 99.5
Ethyl acetoacetate ($CH_3COCH_2CO_2CH_2CH_3$)	Avocado Research Chemicals	≥ 99
Nitric acid (HNO_3)	Aldrich	70
Ammonium hydroxide (NH_4OH)	Aldrich	28-30 (NH_3 basis)
Sodium hydroxide (NaOH)	Aldrich	≥ 98.5
Acetone (CH_3COCH_3)	Aldrich	≥ 99.5
n-Octane ($CH_3(CH_2)_6CH_3$)	Aldrich	≥ 99 (anhydrous)
Urea (NH_2CONH_2)	Aldrich	≥ 99.5

3.2.1.1 Aluminum tri-sec-Butoxide

The sol-gel catalysts synthesized from aluminum tri-*sec*-butoxide were prepared in the same manner as described by Seker (2000). Aluminum tri-*sec*-butoxide was first mixed with the water-ethanol solution and then the necessary amount of chloroplatinic acid of platinum or gold acetate was added into the aluminum sol solution. The obtained gel was dried at 100 °C for 12 h followed by calcination at 600 °C for 24 h.

3.2.1.2 Aluminum Isoproproxide

Desired amount of aluminum isoproproxide was initially dissolved in hot water and kept at 85 °C under agitation for several minutes to form aluminum hydroxide. Then nitric acid was added in order to redisperse the aluminum sol. After stirring the mixture for 1 h under the same temperature, an appropriate amount of the metal precursor either of Pt or Au pre-mixed with a modifier such as 1,3 butanediol was slowly introduced into the system. It was further kept stirring at this temperature for another hour followed by aging at the room temperature overnight. The solvent was removed by low heating under a reduced pressure condition for gelation. Drying at 100 °C for 12 h was applied to the obtained gel followed by calcination at 600 °C for 24 h.

3.2.2 Deposition-Precipitation

The deposition-precipiation technique is an alternative choice to obtain a uniform distribution of small particles over a support. The solution of metal precursor is first mixed with the preformed support into slurry and followed by adding a sufficient alkali solution to cause precipitation of the metal hydroxide. There are two processes involved in the deposition as follows (Perego and Villa, 1997):

1) precipitation from bulk solution or from pore fluids
2) interaction with the support surface

However, rapid nucleation and growth resulting in precipitation in the bulk solution is unwanted. Since it gives the large particles which will be unable to enter into the pores inside the support, but will deposit only on the external surface. This leads to large crystallites and inhomogeneous distribution. Consequently, the precipitation of the metal hydroxide particles on the internal area of the support is prefered in order to obtain a well-dispersed and uniform active phase over the support. Hence, the higher nucleation rate at the surface than that in the bulk solution must be preserved. Homogeneous distribution also occurs when the OH groups of the support interact directly with the metal ion present in the precursor solution. To achieve the best results, it should apply a well mixing process and a slow addition of the basic solution to avoid the local OH^- build up.

Hydrogen tetrachoroaurate (III) hydrate precursor was used with two types of alumina to synthesize gold supported catalyst. First support was gamma alumina supplied from Aldrich. The other was sol-gel alumina prepared from aluminum tri-*sec*-butoxide by the same procedure as previously described except metal precursor adding. The procedure of Ueda *et al.* (1997) was applied in the catalyst preparation. The pH of aqueous solution of gold salt was adjusted to 7.0 by adding 0.1 M of NaOH. Then alumina was introduced to the solution under agitation for 1 h to deposit gold hydroxide on the alumina surface. The precipitate was filtrated and washed several times to eliminate the excess ions. After that the final precipitate was dried at 100 °C for 5 h and calcined at 500 °C for 5 h.

3.2.3 Impregnation

Impregnation is a simple method to prepare the catalysts. This technique is to bring a solution containing active metal precursor in contact with the support material which is subsequently dried to remove imbibed solvent. After that it is activated by the appropriate treatment such as calcination, reduction, etc. There are two methods used in this preparation which are dry and wet impregnation. During impregnation, three processes occur as follows (Anderson and Garcia, 2005):

1) solute transportation to the pore system of the support
2) solute diffusion within the pore system
3) solute uptake by the pore wall

In case of wet impregnation, solute transportation to the outer particle surface is an additional step. Different active phase profiles will be obtained depending on the process conditions during impregnation and drying such as the pH, the temperature, weak or strong support interaction (Pinna, 1998; Campanati *et al.*, 2003).

In this work, dry impregnation (or incipient wetness impregnation) was employed. The support was filled with an active phase solution of which the quantity corresponds to its total pore volume. The same gold precursor and alumina in deposition-precipitation were applied in the synthesis. The sol-gel alumina synthesized from aluminum tri-*sec*-butoxide or the commercial gamma alumina was impregnated by the appropriate amount of hydrogen tetrachloroaurate dissolved in water to achieve the desired amount of gold loading. The same drying procedure was employed followed by 500 °C calcination for 5 h.

After calcinations, all types of catalysts were ground and sieved into 80-120 mesh sizes before activity test.

3.3 Experimental Equipment

The schematic diagram of the experimental apparatus is shown in Figure 3.1 in which it was divided into 3 main parts as follows:

3.3.1 Gas Blending System

The reactant gas mixtures consisted of 0-1,000 ppm NO, 0-14% O_2, 0-1,000 ppm reducing agent (C_3H_6 or urea) and 25 ppm SO_2 (when used) balanced in Helium. Each gas was controlled independently by mass flow controller to achieve an approximate space velocity of 50,000-105,000 $cm^3\ h^{-1}\ g^{-1}$. Water was introduced to the system by passing the gas mixtures through a bubbler at the room temperature to obtain around 2-3% moisture in gas stream. The humid stream route was heated to avoid water condensation. Either bubbler or injection pump was employed to deliver urea to the system. In the former method, the reactant gas mixtures were sent in the same manner as water delivery through the bubbler containing 1.4 wt% urea aqueous solution. In the latter method, 1.4 wt% of urea aqueous solution was transferred to the system by a peristaltic tube pump; supplied from Cole Parmer, at the appropriate flow rate to achieve the desired portion in the reactant gas mixtures. When octane was used as a reducing agent, it was introduced to the system by passing helium gas through the saturature. It contained octane liquid which was controlled at the right temperature to achieve the desired concentration range.

3.3.2 Reactor

The catalytic activity was studied over a fixed bed microreactor at the atmospheric pressure. The catalyst was placed between two quartz wool layers in a quartz U tube reactor, 3 mm ID. The reaction temperature was electrically heated from 150 to 500 °C with a 50 °C increment. It was controlled by a PID temperature controller; a Yokogawa instruments model UP27, equipped with a chromel-alumel thermocouple of which tip was located right on the top quartz wool layer on the fixed bed catalyst.

3.3.3 Analytical Instrumentation

Product analysis was performed after the reaction reached a steady state condition; at least 1 hour time on stream. The outlet stream from the reactor was removed water out by passing through a membrane dryer supplied from Perma Pure Inc. Then the dehydrated effluent gas was qualitatively and quantitatively analyzed by the following instruments.

3.3.3.1 NO_x Chemiluminescence Analyzer

Nitric oxide (NO) and nitrogen dioxide (NO_2) were determined by a Thermo Environmental 42CHL NO_x chemiluminescence analyzer. The sample gas was mixed with ozone, which was generated from dry air or oxygen, in the reaction chamber. Consequently, NO reacted with O_3 to form NO_2. Some electronically excited NO_2 were produced. These molecules returned to their ground energy level by giving off energy in the form of light emission (chemiluminescence) with intensity linearly proportional to the concentration of NO. These processes was delineated by Clough and Thrush (1967) as the equations below:

$$NO + O_3 \rightarrow NO_2^{*} + O_2 \qquad (3.1)$$

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (3.2)$$

$$NO_2^* \rightarrow NO_2 + h\nu \qquad (\sim 600\text{–}3{,}000 \text{ nm}) \qquad (3.3)$$

The chemiluminescence resulted from the reaction was monitored through an optical bandpass filter by a high sensitivity detector; photomultiplier tube (PMT), located at the end of the reaction chamber. After that, an electronic package took the output signal from the detector and processed it to voltage, current level, or digital signal. Finally, it was reported to NO-NO_2-NO_x quantities.

The sample inlet generally had two flows modes. The first one; NO mode, was a direct path of sample to the reaction chamber. Ideally, only the NO in the sample reacted with the ozone to produce light emission. The other one; NO_x mode, was routed through a converter that transformed the NO_2 to NO before further delivery to the reaction chamber. The different signal between these two modes was interpreted to the corresponding NO_2 portion.

3.3.3.2 Gas Chromatography (GC)

A gas chromatography is an instrument used to separate the mixtures. In the chromatographic separation, the sample is transported in a mobile phase which is gas in this case. This mobile phase is then forced through an immiscible stationary phase that can be a liquid or solid fixed in a column or on a solid surface. The sample will be introduced to the chromatographic system via an injector. Its component which strongly interacted with the staionary phase will be retained in the column so that it will take time longer to travel through the column. On the other hand, the component which is weakly held will move relatively rapidly. After each component leaves the column, it will be carried by carrier gas to the detector where data is collected and sent out as a signal. It will be further processed and reported as a chromatogram. The observed peaks were identified by the retention time in comparison with those of the standard gases. While the composition of the effluent gas was quantitatively determined from the peak area by using calibration curve as a reference.

The effluent gas from the reactor was analyzed by a SRI 8610C gas chromatograph equipped with a helium ionization detector (HID) and a thermal conductivity detector (TCD) or by a Hewlett Packard 5890 series II gas chromatograph equipped with thermal conductivity detector (TCD). Product gases were separated in an appropriate column such as a 36 ft long HayeSep DB column, a 6 ft long Porapak N column to further analyze its composition both qualitatively and quantitatively.

3.3.3.3 Fourier-Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy reveals the information about the vibrational states of a molecule. IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). Intensity and spectral position of IR absorptions allow the identification of structural elements of molecule. Typical vibrations of functional groups can be determined by this method. As well as in the gas phase, a rotational fine structure can often be observed from the moment of inertia of the molecule. When a spectrum is recorded using a conventional, dispersive IR spectrometer, each data point reveals the transmitted light at the respective frequency. The signal provided by the FTIR technique contains information about the complete spectrum of the probe. This signal will be transformed from the time-domain into the frequency-domain in order to give the spectrum. This transformation is so called Fourier transformation.

The relationship between the amount of the radiation absorbed or transmitted and the concentration of the sample at a particular wavelength is known as Beer's law (Szymanski, 1964) as given below:

$$A = \log \frac{1}{T} = \log \frac{P_0}{P} = abc$$

where

A = absorbance
T = transmittance
P_0 = the amount of radiation of one wavelength incident on the sample
P = the amount of transmitted by the sample
a = absorptivity
b = the path length in the sample
c = the concentration of the sample

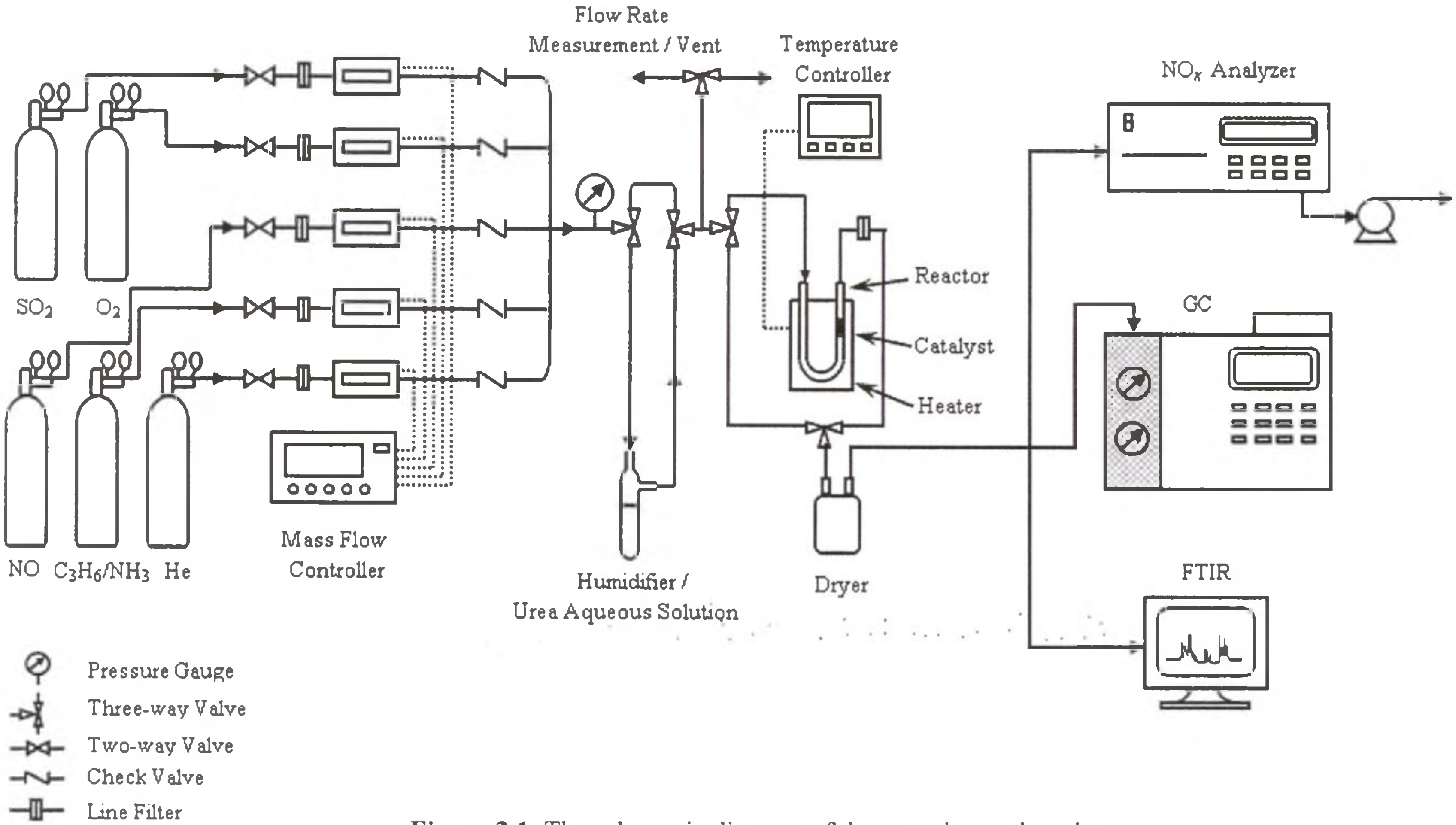

Figure 3.1 The schematic diagram of the experimental equipment.

In this work, carbon monoxide (CO), carbon dioxide (CO_2) and nitrous oxide (N_2O) were analyzed by a Mattson Galaxy 7020 A Fourier-transform infrared spectroscopy (FTIR) equipped with a 10 cm path length gas cell. This instrument is an interferometer equipped with potassium bromide (KBr) beam splitter and mercury cadmium telluride (MCT) detector, which is kept at 77 K with liquid nitrogen. MCT detector measures the transmitted IR coming out of the sample gas cell. A moving mirror and a fixed mirror together with the beam splitter inside the instrument create an interference pattern. The result is the IR intensity versus the position of the moving mirror, which is determined by a He-Ne laser. It is called an interferogram. Then a Fourier transform procedure performed in the electronics of the instrument converts the interferogram into the intensity versus frequency. Then the gas spectra were analyzed by WinFirst software version 3.61 giving the information of molecular structures and the corresponding quantities.

3.4 Catalytic Activity Measurement

3.4.1 Activation Process

Before testing, activation process was applied for the fresh catalysts. The catalysts were kept at the temperature from 100 to 500 °C with the 50 °C increment under the flow rate of 77 ml/min of wet reactant gases stream, consisting of 750 ppm NO, 750 ppm C_3H_6 and 7% O_2 balanced in He. They were held at each temperature for 1 hour and kept overnight once the temperature reached 500 °C. This heat treatment cycle was employed until the catalysts reached their stable activity levels.

3.4.2 Activity Testing Procedure

After the cataysts were activated, they were examined the activity at the atmospheric pressure and the temperature ranging from 100 to 500 °C under wet and dry reactant gas mixtures. The different reducing agents were employed in this study. Either C_3H_6, urea or NH_3 was used in each test. The water containing in the outlet gases was trapped by a condenser and a water selective membrane dryer from Perma Pure Inc. In addition, the effluent gases were passed through the phosphoric acid to eliminate NH_3 and HNCO when urea or NH_3 was used as a reducing agent. The dehydrated stream was subsequently determined the composition by analytical instrumentation; NO_x analyzer, GC, and FTIR.

3.4.3 Conversion and Selectivity Calculation

3.4.3.1 Hydrocarbon Conversion

The hydrocarbon conversion was defined as:

$$\frac{(\text{ mole of CO} + \text{mole of } CO_2)}{(\text{ n x mole of } C_nH_m)} \times 100\%$$

3.4.3.2 NO_x Conversion

The NO_x conversion was defined as:

$$\frac{(\text{ mole of } NO_{in} + \text{mole of } NO_{2\,in}) - (\text{ mole of } NO_{out} + \text{mole of } NO_{2\,out})}{(\text{ mole of } NO_{in} + \text{mole of } NO_{2\,in})} \times 100\%$$

3.4.3.3 N_2 Selectivity

The N_2 selectivity was defined as:

$$\frac{\text{mole of } N_2 \text{ product x 2}}{(\text{ mole of } NO_{in} + \text{mole of } NO_{2\,in}) - (\text{ mole of } NO_{out} + \text{mole of } NO_{2\,out})} \times 100\%$$

3.5 Catalyst Characterization

The physical and chemical properties of the catalysts were examined by some characterization techniques to understand more about the catalytic behavior. The following techniques were applied in this work.

3.5.1 BET Surface Area Measurement

Most heterogeneous catalysts are porous solids. The porosity arises from the preparation methods. Typically, the catalysts contain one or more groups of pores whose size and volume depend on preparation method. Surface area, pore size, pore size distribution, pore structure, and pore volume of the carrier are the important factors of catalytic activity because the active sites are present or dispersed throughout the internal surface through which reactants and products are transported. The size and number of pores determine the internal surface area. High surface area maximizes the dispersion of active components that benefits the reaction. However, the diffusion resistance of reactants or products grows if the pore size is too small. The pores are classified in different classes depending on their sizes (Leofanti *et al.*, 1997):

1) micropore ($\phi < 2$ nm), molecular diffusion
2) mesopore ($2 < \phi < 50$ nm), Knudsen diffusion
3) macropore ($\phi > 50$ nm), bulk diffusion

The Brunauer-Emmett-Teller method (BET) was used to determine the surface area and the pore size. BET surface area was measured with a Micromeritics 2010 instrument. About 0.1 g of catalyst sample was degassed under vacuum at 300 ^{o}C until the pressure inside the sample tube reached around 5 μmHg steady state. Then N_2 adsorption was proceeded at 77 K. A standard Micromeretics program was employed to calculate both BET surface area and BJH pore size distribution.

3.5.2 X-ray Diffraction (XRD)

Approximate crystallite size and phases present in the catalysts were determined by X-ray diffraction, Riguku powder diffractometer, operated at 40 kV and 100 mA with Cu Kα radiation. The average size was calculated by the Debye-Scherrer equation (Niemantsverdriet, 1993). However, this technique has some limitations. Amorphous phase and small particles give either broad and weak diffraction lines or no diffraction at all. Hence, the particle size ranges below 5 nm can not be determined. Furthermore, large crystallite sizes above 50 nm give sharp peak so that the change in peak shape is small leading to insensible in calculation

(Anderson and Pratt, 1985). In practical, cystallite size ranged 5-50 nm can be calculated by applying the Debye-Scherrer equation as shown below:

$$L = \frac{K\lambda}{B\cos\theta}$$

where

L = a measure for the dimension of the particle in the direction perpendicular to the reflecting plane

B = the width at half peak height

λ = X-ray wavelength, 0.154 nm for Cu Kα radiation

θ = diffraction angel

K = a constant, usually equal to 1

3.5.3 High Resolution Transmission Electron Microscopy (HRTEM)

In transmission electron microscopy, a thin sample is subjected to a beam of electrons. The ability to pass through the object gives the different contrast of image. The dense areas in the sample inhibit electron transmission giving the dark spots on the film. Therefore, metal particles can be determined from the dark spot outline. This technique also offers the particle size distribution information.

JEOL 4000 HRTEM was used to determine Pt and Au particle size and their distributions. The catalyst powder was ground in *i*-propyl alcohol and subsequently kept in a sonic bath for 15 min. A drop of the alcohol powder suspension was put on a holly carbon-coated copper screen and then alcohol was evaporated at room temperature under vacuum before transferring to HRTEM column. An amount of 90-200 crystallites pictures for each catalyst were collected spatially over holly carbon coated copper screen to find the crystallite size distribution (Seker *et al.*, 2002).

3.5.4 Neutron Activation Analysis (NAA)

The neutron activation analysis technique was employed at the Ford Nuclear Reactor at the University of Michigan to find the gold amount in the catalysts. The concentration of gold in alumina matrix was determined through direct comparison to the standard reference material NBS-SRM-2128-1 (1 ± 0.01% Au). Approximately 100 mg of the liquid standard was placed on thin strips of filter paper in polyethylene vials, the mass recorded to the nearest 0.1 mg, and the standards dried to constant weight. Similarly, an approximate 10 mg of the samples was prepared. Samples and standards were irradiated in position L10D (with an average thermal neutron flux of ca. 3.9×10^{11}) for 1 h, and were rotated during irradiation to ensure equal exposure to neutron flux. After irradiation, the resulting gamma activity in each vial was counted using a high purity germanium (HPGe) detector for 5,000 s. The resulting in peak areas with associated errors of less than 1% gold concentrations in the unknowns were based on the decay-corrected gamma activity per milligram averaged across four standards, while a fifth replicate was served as a check standards for quality control. The check standard indicated a total measurement error of ca. 0.04% (Seker *et al*., 2002).