Preparation, Characterizations and Reaction
of
Bimetallic Catalyst for Reforming

By:

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Dissertation submitted in partial fulfillment of
The requirements for
Bachelor of Engineering (Hons)
(Chemical Engineering)

November 2004

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Certification of FYP Final Draft Submission

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Thank you.

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CERTIFICATION OF APPROVAL

Preparation, Characterization and Reaction of Bimetallic Catalysts for Reforming

By

Marlinne Goven

A project Dissertation submitted to the
Chemical Engineering Program
Universiti Teknologi PETRONAS
In partial fulfillment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and the acknowledgements, and that original work contain herein have not been undertaken or done by unspecified sources or persons.

(MARLINNE GOVEN)

ABSTRACT

This study has been done to characterize the bimetallic catalysts which consist of the Pt-Re/Al_2O_3, Pt-Sn/Al_2O_3 and Re-Sn/Al_2O_3 catalysts by using temperature programmed reduction (TPR). For comparison, the support (γ-Al_2O_3), the monometallic catalysts (Pt/Al_2O_3, Re/Al_2O_3 and Sn/Al_2O_3) and the tri-metallic catalyst (Pt-Re-Sn/Al_2O_3) were also being characterized by using the same technique.

Platinum-on-alumina catalyst had been introduced to the industry in 1949 since it have dual function of providing both the acidic sites and metallic sites that are important for reforming reaction. Beginning in 1970s, it was introduced as having one or more additional metallic components including rhenium and tin. These bimetallic catalysts exhibit greatly improved stability (cycle length) and selectivity.

The TPR analysis is based on the reducibility of species in the solids which enables one to obtain information not only of a purely analytical nature but also and more importantly, about the condition of species present in and on solids. This technique allows the determination of the temperature at which the reduction itself takes place as the function of the flows conditions, the percentage of a reactive gas, the quantity of samples and the speed of the temperature increase.

Based on the TPR analysis, bimetallic catalysts and the tri-metallic catalysts are observed to have lower reduction temperatures than the monometallic catalysts and are concluded to have better catalytic activity. The temperature at which reduction occurs and the number of reduction peaks depend on the oxidation state of the metals, the interaction of the oxides among them and with the support and on the possible catalytic action of Pt or other elements present or generated during reduction. The significance of low reduction temperature is it indicates a better activation capability therefore considered good and effective for the industry.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 Background of study

Catalysis plays important roles in the economy, environment and public health of the nations. It is impacting human lifestyle in various ways where fuels that powered the vehicles, the clothes that we wore and food that we ate have gone through catalytic process. Much of our present-day catalyst technology are predominantly used in the activity of petroleum refining and chemical production where both industries account for 97% of total catalyst usage and the rest are use in the environmental cleanup. However, few trends are going to be observed in the future such as milder reaction conditions, emergence of new catalysts and materials and innovations in contacting and reactor designs. An example of the new catalysts that had gain acceptance by the industry are the multifunctional bimetallic catalysts such as the Pt/Re and Pt/Sn which had already in used in the petroleum refining. Realizing the promising value of these catalyst to the industry, further research still need to be done and this project is specifically aim to study the bimetallic catalyst system of few selected catalysts in term of preparation, characterization and the reaction.

1.1.1 Definition of catalysts

There are many ways to define a catalyst but generally, catalyst is a substance that increases the rate of reaction without being appreciably consumed in the process. However, Gates, Katzer, and Schuit in their book of Introduction to Catalysis had mentioned that one need to be careful with this definition since surface structure could change significantly during the reaction, but there is no stoichiometric relationship between this change and the overall stoichiometry of the reaction. Another thing needs to be noted is that a catalyst can not change the ultimate equilibrium of a reaction as determined by Thermodynamics; rather, it accelerates the approach to equilibrium.

1.1.2 Classifications of Catalysts

Hagen (1999) had classified catalysts into three types:

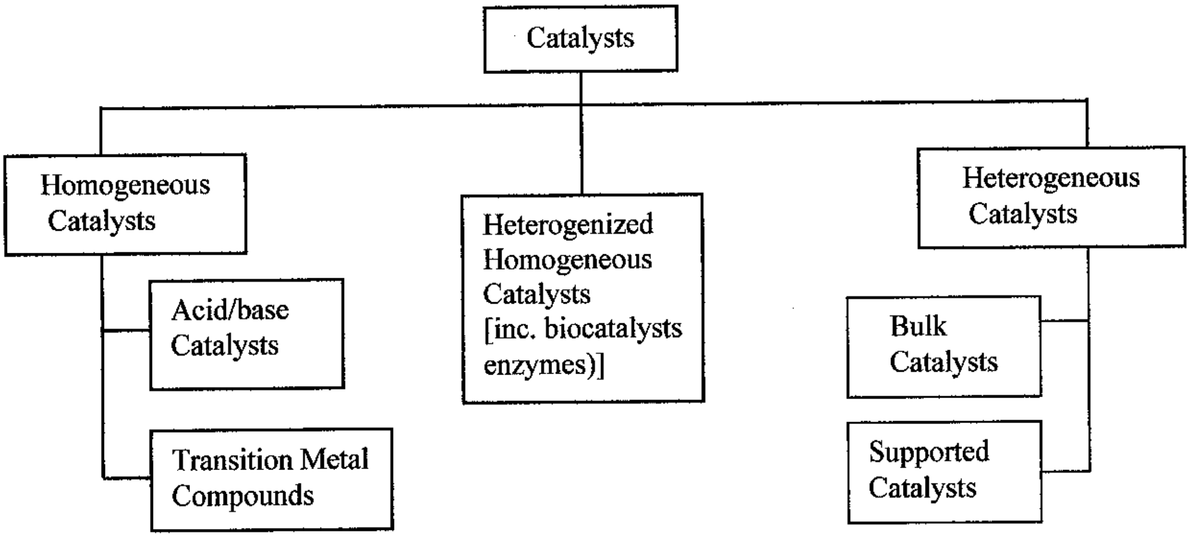


Figure 1.1: The Classification of Catalysts

However, the forms that are widely used are

a) Heterogeneous Catalysts

b) Homogeneous Catalysts

The comparisons between these two forms are presented below:

Table 1.1: Comparison between heterogeneous and homogeneous catalysts

Conditions	**Heterogeneous Catalysts**	**Homogeneous Catalysts**
Separation	Easy (Simple physical means)	Difficult
Thermal Stability	High	Low
Selectivity	Less selective, contains many different sites	More selective contains only one type of active site
Activity	Less active, only surface atoms are exposed	More active, all active sites are exposed
Reaction Condition	Requires high temperature and can perform over wide range of condition	Mild temperature and narrow range of condition
Reaction Rate	Reduces when problems with diffusion in the pore system arise	Reduces when problems with solubility arise
Physical rate	Solid-gas Solid-liquid	Liquids (Reactants must be in stable solution)
Deactivation	Poison molecules can block a pore containing many active sites (pore plugging)	One poison molecules deactivates one metal complex
Catalyst system	Complex surfaces, reaction mechanism is more difficult to understand	Well defined system with simpler mechanism

1.1.3 Catalyst Materials

Heterogeneous types of bimetallic catalysts are being focused in this study. The make-up of typical heterogeneous catalysts comprised:

- *Active Catalytic Phase* – The active catalytic phase is usually dispersed in the pores of supports in the form of micro crystallites of 1 – 50 nm

- *Promoter* – A promoter is added in order to increase the activity and/or stability. For example, it is added in 1 - 5 % to enhance and/or maintain the texture or to chemically increase the catalytic activity.
- *High surface area carrier (support)* – This is to facilitate the dispersion and stability of the active catalytic phase.

Farrauto and Bartholomew (1997) had summarized the components of a typical heterogeneous catalyst in the table below:

Table 1.2: Components of typical heterogeneous catalysts: material types and examples

Component	**Material Types**	**Examples**
Active Phase	Metals	Noble metals (Pt, Pd) ; base metals (Ni, Fe[a])
	Metals Oxides	Transition metal oxides (MoO_2, CuO)
	Metal Sulfides	Transition Metal Sulfides (MoS_2, Ni_3S_2)
Promoter Textural	Metal Oxides	Transition metal and Group IIIA (Al_2O_3, SiO_2, MgO, BaO, TiO_2, ZrO_2)
Chemical	Metal Oxides	Alkali or alkaline earth (K_2O, PbO)
Carrier (or support[b])	Stable, high surface area metal oxides, carbons	Group IIIA, alkaline earth and transition metal oxides (Al_2O_3, SiO_2, MgO) zeolites and activated carbon

1.1.4 Catalyst Properties

Properties can be classified as:

- *Dynamic* – behavior during reaction
- *Chemical* – Chemical state of the active catalytic phase, acidity, surface composition and structure
- *Physical* – surface area, pore structure, density and mechanic properties (e.g. crush strength)

a *Dynamic Properties*

The dynamic properties of catalysts include the activity, selectivity and stability. The definitions of these important properties are listed in Table 2.4 which is adapted from Farrauto and Bartholomew (1997)

Table 1.3: Dynamic (catalytic) properties of catalysts: Definitions and specifications

Property	**Definitions/Specification**
Intrinsic specific activity	Specific reaction rate based on the surface area or number of sites measured in the absence of heat/ mass transport and deactivation disguises at specified T, $P_{reactants}$, and conversion
Turnover frequency	Molecules converted or produced per catalytic SA per second
Specific rate (SA based)	Moles converted or produced per catalytic SA per second
Catalytic activity	Reaction rate or equivalent measured at specified T, P_{react}, conversion
Rate based on SA	Rate based on catalytic surface area, intrinsic or nonintrinsic
Rate based on mass, volume	Rate based on catalysts mass or volume, intrinsic or nonintrinsic
T for required conversion	Temperature for required conversion of reactants, usually nonintrinsic
T for given product quality	Temperature for specified product quality, usually nonintrinsic
Selectivity	Amount or relative rate of production of specified product related to others
Rate based	Rate of production of specified product divided by rate for another product
Product Distribution-Based	Percentage of specified product in total product mixture
Stability	Measure of activity decline at specified conditions
Deactivation Rate	Rate of activity loss, *da/dt* where *a* is normalized activity
Resistance	Inverse of deactivation rate, e.g. half-life or time to reach specified activity
Tolerance	Residual activity after complete poisoning

b Chemical Properties

Chemical properties of catalysts include the catalyst acidity, composition (surface and bulk), oxidation state (surface and bulk) of the catalytic phase, and structure (surface and bulk). These properties are summarized in Table 2.3 below:

Table 1.4: Chemical properties of catalysts: definitions and specifications

Property	Definitions/Specifications
Acidity	
Bronsted acidity	Ability of a material to donate protons
Lewis acidity	Ability of materials to capture electrons
Chemical Composition	Chemical make-up by element
Bulk	
Surface	
Oxidation state	Chemical state or valence state
Bulk	
Surface	
Chemical Structure	Geometric arrangement of atoms, arrangement and properties of electrons, and bonding characteristics of atom
Bulk	
Surface	

c. Physical and Mechanical Properties of Catalysts

Farrauto and Bartholomew (1997) listed the definitions and specifications of physical and mechanical properties of catalysts. The physical properties include the particle size, density pore volume, porosity, pore size and pore size distribution, BET surface area, active site concentration (catalytic surface area), and dispersion. The mechanical properties included crush strength and attrition resistances.

Table 1.5: Physical and Mechanical properties of catalysts: Definitions and Specifications

Property	**Definitions/Specifications**
Density	
Bulk Density, ρ_b	Mass perunit vol. of bulk catalysts, i.e. bed, packed density
Particle Density, ρ_p	Mass perunit vol. of pellet; also called apparent density
Solid Density, ρ_s	Mass perunit vol. of solid; also called skeletal or true density
Pore Volume, V_{pore}	
Macropore volume	Volume of macropore perunit mass ($d_{pore} > 50$ nm)
Mesopore volume	Volume of mesopore perunit volume (d_{pore} of 3-50 nm)
Micropore volume	Volume of micropores perunit mass ($d_{pore} < 3$ nm)
Pore size and size distribution	
Macropores	Average size (diameter) and distribution for $d_{pore} > 50$ nm
Mesopores	Average size (diameter) and distribution for d_{pore} of 3 - 50 nm
Micropores	Average size (diameter) and distribution $d_{pore} < 3$ nm
Surface area (SA), S_{int}	
Meso and Macropores	SA of pores with diameters of 3-5000 nm
Micropores	SA of pores with diameters of less than 3 nm
Active site concentration or SA, S_{cat}	Number of active sites per mass of catalysts or active SA
Catalyst particle size	diameter and/or length of pellets/ extrudates or holes size (pitch) of monoliths
Crushing strength	
Particle	Force necessary to crush particle in axial or radial direction
Bulk	Displacement or percentage of fines versus hydraulic pressure
Attrition	Percentage loss per time due to tumbling

1.1.5 Catalyst Deactivation

The condition where a catalyst may lose its activity and selectivity over times is known as deactivation. Four general causes of this are:

i. *Poisoning* – An impurity in the feed (e.g. sulfur) reduces activity/selectivity

ii. *Fouling* – A physical blocking of active sites by solid material (e.g. coke)

iii. *Sintering* – Physical process leading to reduced catalytic surface area (e.g. attrition)

iv. *Loss of Active Species* – A surface reaction takes place in which the active surface species is converted into a non-active species.

1.1.6 Catalyst preparation and forming

Generally, the finished catalysts are made via three approaches (listed in decreasing orders of importance):

i. Deposition of the active component onto a carrier by impregnation, adsorption, ion exchange or precipitation followed washing, drying, calcinations and activation

ii. Precipitation of a complex high surface area oxide or carbonate containing the active component following by drying, calcinations and activation

iii. Preparation of a dense, nonporous compound or alloy containing the active component followed by extraction of material leaving a porous, high surface area active phase.

General schemes illustrate typical routes for catalyst preparation and forming is shown below:

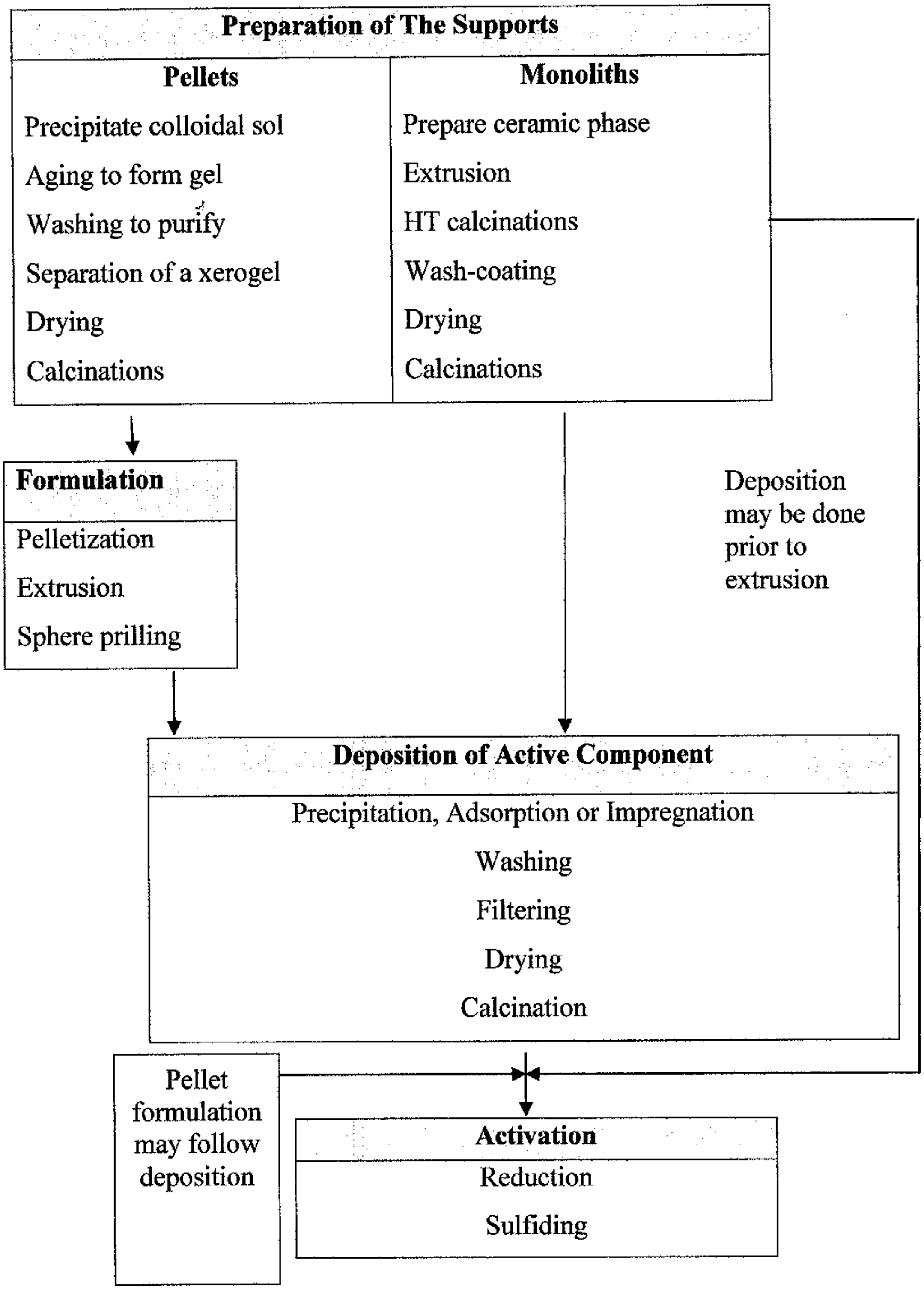


Figure 1.2: General schemes for catalysts preparation and forming.

1.2 Problem Statement

The aim of this project is to study the preparation and the characterizations of few bimetallic catalysts systems used in the industry and their reactions. The characterizations methods will depend on the availability of the equipment in the UTP laboratory.

1.3 Objective(s) of Study

- To study the bimetallic catalysts system
- To study the preparation methods of these catalysts
- To study the characterization method of these catalysts
- To study the reactions catalyzed by these catalysts

1.4 Scope of Study

- Doing a literature review on the bimetallic catalysts
- Characterizing the bimetallic catalysts system

1.5 Feasibility of project

The project is feasible to be finished within the time frame because the scope has has been narrowed down to the characterization of the bimetallic catalysts system only by using Temperature Programmed Reduction method.

CHAPTER 2

LITERATURE REVIEW

2.1 Catalytic Reforming

Rase (2000, pg. 301) explained that the catalytic refining converts low-octane naphtha streams (20-50 RONC) to high octane (90-108 RONC) gasoline blending stock using a dual function catalysts with both metallic sites of Pt (or Pt with other metals as promoters) and acid sites supplied by the alumina support. The traditional feed is heavy naphtha (primarily paraffin and naphthenes, 200 °F – 400 °F, 93 – 204 °C BP) from atmospheric distillation of crude oil. Naphtha from delayed coking and hydro cracking and other streams high in naphthenes are also used.

The first catalytic reforming process, which used molybdenum oxide-on-alumina catalysts, was jointly developed in 1939 by Standard Oil of New Jersey (Exxon), Standard of Indiana (Amoco) and M.W. Kellogg Company. UOP introduced the first process (Platforming™) using platinum-on-alumina as a dual-function catalyst having both acidic sites and metallic sites in 1949 and it soon become the catalyst of choice.

After the primary patents expired, a number of the merchant catalysts are now available, often based on new promoters and other unique innovations. Platinum remains the major active component of all modern naphtha reforming catalysts. But beginning in the 1970s, catalysts were introduced as having one or more additional metallic components including the rhenium, iridium and tin. These bimetallic catalysts and multimetallic catalysts exhibit greatly improved stability (cycle length) and selectivity.

2.2 Catalysts Used

The bimetallic catalysts used in this experiment are comprised of the combination of three metals:

- Pt-Re/Al_2O_3
- Pt-Sn/Al_2O_3
- Re-Sn/Al_2O_3

However, to make a comparison for all these catalysts: the support, the supported monometallic catalysts and the tri-metallic catalysts had also been added to the scope of study:

- Al_2O_3
- Pt /Al_2O_3
- Re/Al_2O_3
- Sn/Al_2O_3
- Fresh Al_2O_3
- Pt-Re-Sn/Al_2O_3

The metal loading of all the catalysts are 1 wt%.

2.2.1 Pt-Re/Al_2O_3

Rase (2000) had mentioned that the platinum-rhenium catalysts are the most widely used for the catalytic reforming process because they are more coke tolerant and thus provide longer cycle times (times between regeneration). In addition, it has also been possible to reduce operating pressure and take advantage of yield enhancing equilibrium conditions and energy savings while maintaining attractive cycle times.

Sintering of Platinum is mainly influenced by high temperature. Rhenium metals serving as the second metal in the bimetallic catalysts apparently acts as barriers to the sintering of Pt by virtue of their effect on Pt interaction with the alumina. Thus, although the Pt on the bimetallic catalyst does not sinter, it does so more slowly or at higher temperatures. Typically, a Pt-Re catalyst will have two to four times the cycle times of a platinum-only catalyst. The suppliers for these catalysts are Acreon, Criterion, Indian Petrochem., Inst. Mexicano Petrol, Kataleuna, UOP LLC and Procatalyse. Meanwhile, the licensors of this catalyst are Exxon Research and Engineering, Howe Baker, IFP and UOP LLC.

2.2.2 Pt-Sn/Al_2O_3

This catalyst can be used for the Naphtha reforming process as well. However, the Sn does not protect Pt from the coking as Re does. It required frequent regeneration and used, therefore, in continuous regeneration units, the operating pressure is at 50 psig. Another source had mentioned that this catalyst is also significant for the methylcyclohexane as a vector for hydrogen storage that is requires for an effective dehydrogenation catalyst.
(http://.www.editionstechnip.com/sources)

2.2.3 Re-Sn/Al_2O_3

This catalyst is used to hydrogenate fatty acids or their methyl esters, to produce fatty alcohols, at high temperature but low pressure (50 bars). The presence of tin in the catalysts has been found to be the instrumental preserving carbon-to-carbon double bonds in the fatty acids chains.
(http://www.mpopc.org.my/ebtenfu.html)

2.2.4 *Pt/Al_2O_3*

The platinum-on-alumina catalyst was introduced after World War II for naphtha reforming. This catalyst, which was also used in dehydrogenation reactions, was found to deactivate relatively fast due to coke formation. A large number of different bimetallic platinum catalysts, with and without promoters, have been studied in order to find a catalyst more stable against deactivation than pure platinum on alumina. Platinum-supported catalysts are used in the refining of crude oil, reforming, and other processes used in the production of high-octane gasoline and aromatic compounds for the petrochemical industry. (http://www3.interscience.wiley.com/cgi-bin/summary/)

2.2.5 *Re/Al_2O_3*

Rhenium is used in the petroleum industry to make lead-free gasoline. In this application, rhenium compounds act as catalysts. Substitutes for rhenium as a catalyst are being researched. Iridium and tin have been found to be a good catalyst for at least one reaction. Cobalt, tungsten, platinum and tantalum can be used in some of the other applications for rhenium. (http://www.mii.org/Minerals/photorhenium.html)

2.2.6 *γ - Al_2O_3*

(Farrauto, 1997) Support type of γ - Al_2O_3 is the most widely used commercial catalysts carrier because of its most moderately high surface area, thermal stability over a wide range of temperatures relevant to the catalytic process (up to 900 °C), and its ability to be formed into mechanically stables extrudates or pellets. Because of its moderate acidity, it also finds application as a catalyst in a number of reactions requiring the acid sites, e.g. the alkylation of phenol, the dehydration of formic acid, the isomerization of the methylcyclohexane, catalytic reforming, catalytic cracking, polymerization, hydrogenation and the Caluss reaction to produce elemental sulfur from H_2S.

2.2.7 *Sn/ Al_2O_3*

Tin oxide is one of the components of a number of binary oxide systems which find extensive use as catalysts in industry, particularly petrochemicals; the other oxides most commonly used in association are those of vanadium, antimony, molybdenum and phosphorus. These catalysts are employed in the manufacture of various chemical intermediates.

The ability of tin oxide to oxidize carbon monoxide has also led to air purification applications, for example in submarines and safety masks. Both inorganic and organotin compounds have found industrial application as catalysts in the production of polyurethane foams, the curing of silicone elastomers, and certain other commercial processes. (http:// www.tintechnology.biz/tintechnology/tintechnology)

2.2.8 ***Pt-Re-Sn/ Al_2O_3***

This is the type of catalyst that is widely used in the cracking industry. The multimetallic Pt-Re-Sn/A12O3 catalysts is preferred as the catalysts for the cracking process due to the fact that Pt shows good internal bond breaking properties while the addition of the Re provides high resistance towards the deactivation. The high terminal breaking property of the Re could be reduced by the presence of Sn which may deactivate the hydrogenolysis sites of Re.

2.3 Catalysts Characterizations

The objective of catalysts characterizations is to understand the relationship among physical, chemical and catalytic properties of catalyst. By understanding this relationship the causes of deactivation and the design procedures for regeneration can be elucidate. There are many techniques that are available for the catalysts characterization but their application depends on the properties that need to be study. For examples, the physical properties of the catalysts will required a different characterization technique from the chemical properties.

The focus of this project is to study the surface reactivity of the bimetallic catalysts. Therefore, the suitable characterization technique for this study is the temperature programmed reduction or better known as TPR. According to Jones and McNicol (1986), TPR is a relatively new characterization technique that is used for the characterization of solid materials. This technique is based on the reducibility of species in solids, enables one to obtain information not only of a purely analytical nature but also, and more importantly, about the condition of species present in the solid.

A typical reduction profile is shown in Figure 2.4. The profile usually consists of a series of peaks. Each peak represents a distinct reduction process involving a particular chemical component of the solid. The position of a peak in the profile is determined by the chemical nature and environment of the chemical component, and the area of the peak reflects the concentration of that component present in the solid.

Szynwoska et. al (2003) mentions that there are few parameters that must be optimized in the temperature programmed techniques:

- Rate of flow of carrier gas
- Rate of reactant gas to inert
- Volume of samples

- Mass of catalysts
- Size of catalysts particles
- Geometry of reactants vessels
- Intensity of signal (Type of detector)
- Pressure system

Therefore, some times are needed to find out the best optimize condition to obtain an accurate result.

The TPR technique specifically can provide the information which can be classified with the spectroscopic and x-ray techniques that have been traditionally and currently used to characterize solids.

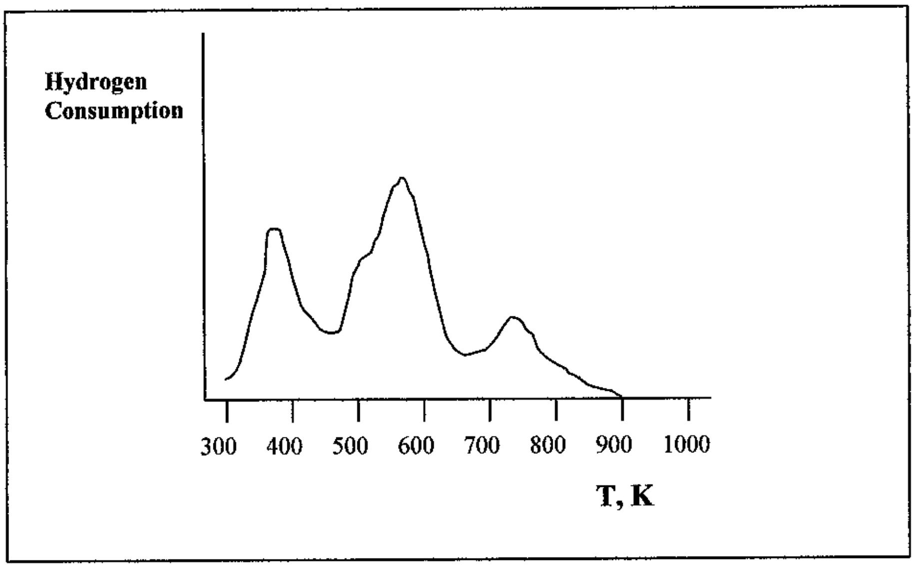


Figure 2.1: A typical reduction profile

Figure 2.2 shows the important characterizations techniques used in 2002 where the temperature programmed technique was among those that are commonly used. Figure 2.3 display the experimental conditions that usually applied in temperature programmed techniques. Basic connections for the apparatus in the temperature programmed scheme are showed in Figure 2.4. The major elements in the figure are a reactor, temperature programmed furnace, purifying system and a dosage system for the carrier gas and reactant gas, a system for chemical analysis. A universal detector in TPD, TPR and TPO is a katharometer; however, mass spectrometer becomes more and more often used. All the figures the explanations for it have been obtained from the journal on temperature programmed techniques by Szynwoska et. al (2003)

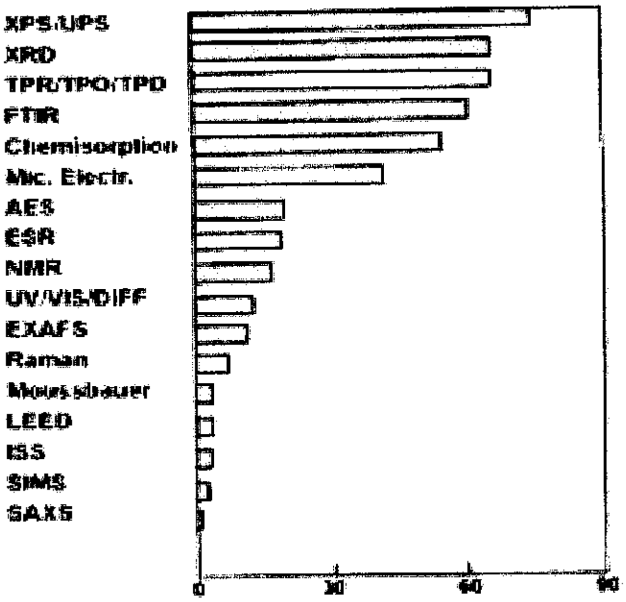


Figure 2.2: Important Characterization Techniques used in 2002

	TPD	TPR	TPO	TPSR
Carrier Gas	Highly pure helium, nitrogen, argon	Highly pure nitrogen	Highly pure helium, nitrogen	Highly pure helium, nitrogen hydrogen
Rate of flow [cm^3/min]	15–60	15–30	30–90	30–60
Adsorbate, reactant	hydrogen	nitrogen + 5% h_2	Helium (nitrogen) + 5% o_2	Reaction dependent
Mass of catalyst [mg]	100–500	100–500	100–500	100–500
Size of particles [mm]	0.025–0.25	0.025–0.25	0.025–0.25	0.05–0.5
Type of reactor	Quartz pipe	Quartz pipe	Quartz pipe	Quartz pipe
Rate of heating [K/min]	10–60	4–60	10–60	10–60
Type of detector	Katharometer, mass spectrometer	Katharometer	Katharometer, mass spectrometer	Flame-ionization katharometer, mass spectrometer, selective detectors
Pretreatment	Catalyst dependent	Catalyst dependent	Catalyst dependent	Catalyst and reaction dependent

Figure 2.3: Experimental conditions used in temperature programmed techniques (mainly metallic catalysts supports on a carrier)

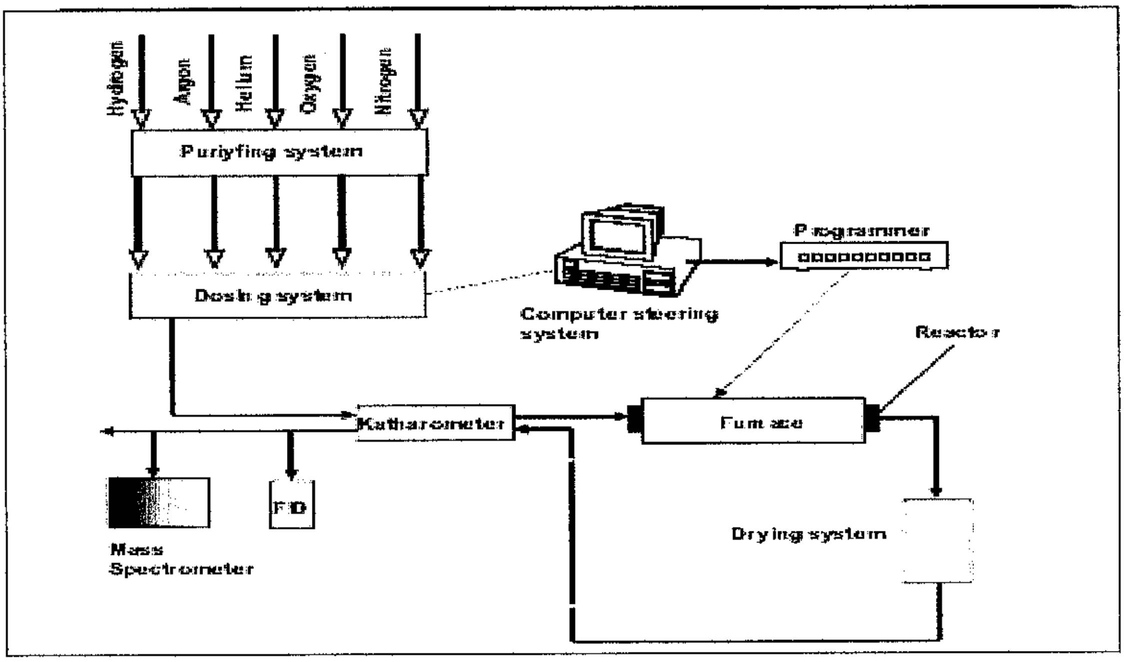


Figure 2.4: The scheme used for temperature programmed techniques.

CHAPTER 3

METHODOLOGY

3.1 Preparation of Catalysts

3.1.1 Chemicals

1. $Pt(NH_3)_4(OH)_2$, from Stream Chemicals, Newburyport USA
2. Re_2O_7, from Stream Chemicals, Newburyport USA
3. $SnCl_2.2H_2O$ from Analar® BDH Limited Poople England
4. γ-Al_2O_3, from Merck, KgaA, Germany

3.1.2 Procedures

The catalysts which are 1 wt% Pt/Al_2O_3, 1 wt% Re/Al_2O_3, 1 wt% Sn/Al_2O_3, 1wt% Pt-Re/Al_2O_3, 1 wt% Pt-Sn/Al_2O_3, Re-Sn/Al_2O_3 and 1 wt% Pt-Re-Sn/Al_2O_3 were prepared by wet impregnation method using $Pt(NH_3)_4(OH)_2$, Re_2O_7 and $SnCl_2.2H_2O$ and γ-Al_2O_3, by another student. The catalysts were dried at 120 °C in oven for 16 hours. Then, they were calcined at 400 °C for 1 hour and kept in a desiccator with silica gel prior to further addition of other metallic catalysts. The purpose of calcining the catalysts was to remove the any impurities like water molecules or organic hydrocarbons (activation process). Refer to Figure 3.1 for the simplified steps for preparing and pretreatment of the Pt-Re-Sn/Al_2O_3 catalysts. Table 3.1, 3.2, 3.3 and 3.4 list the amount of precursor, support and distilled water required to prepare the catalysts.

Table 3.1: Amount of Chemicals required to prepare 1 wt% Pt/Al_2O_3 (0.10g Pt)

Chemicals	**Weight**
$Pt(NH_3)_4(OH)_2$/g	0.6828
γ-Al_2O_3 /g	39.60
H_2O/ml	60.0
Total catalyst weight/g	40.0

Table 3.2: Amount of chemicals required to prepare 1 wt% Re/Al_2O_3 (0.10g Re)

Chemicals	**Weight**
Re_2O_7/Al_2O_3	5.0
Al_2O_3 /g	9.90
H_2O/ml	10.0
Total catalyst weight/g	10.0

Table 3.3: Amount of chemicals required to prepare 1 wt% Sn/Al2O3 (0.10g Sn)

Chemicals	**Weight**
$SnCl_2.2H_2O$/g	5.0
Al_2O_3 /g	9.90
H_2O/ml	15.0
Total catalyst weight/g	10.0

Table 3.4: Amount of chemicals required to prepare 1 wt% Pt - 1 wt% Re – 1 wt% Sn/Al_2O_3 (0.1g Pt – 0.10g Re – 0.10g Sn)

Chemicals	**Weight**
$Pt(NH_3)_4(OH)_2$/g	9.8
Re_2O_7/Al_2O_3	5.0
$SnCl_2.2H_2O$/g	0.190
H_2O/ml	10.0
Total catalyst weight/g	10.0

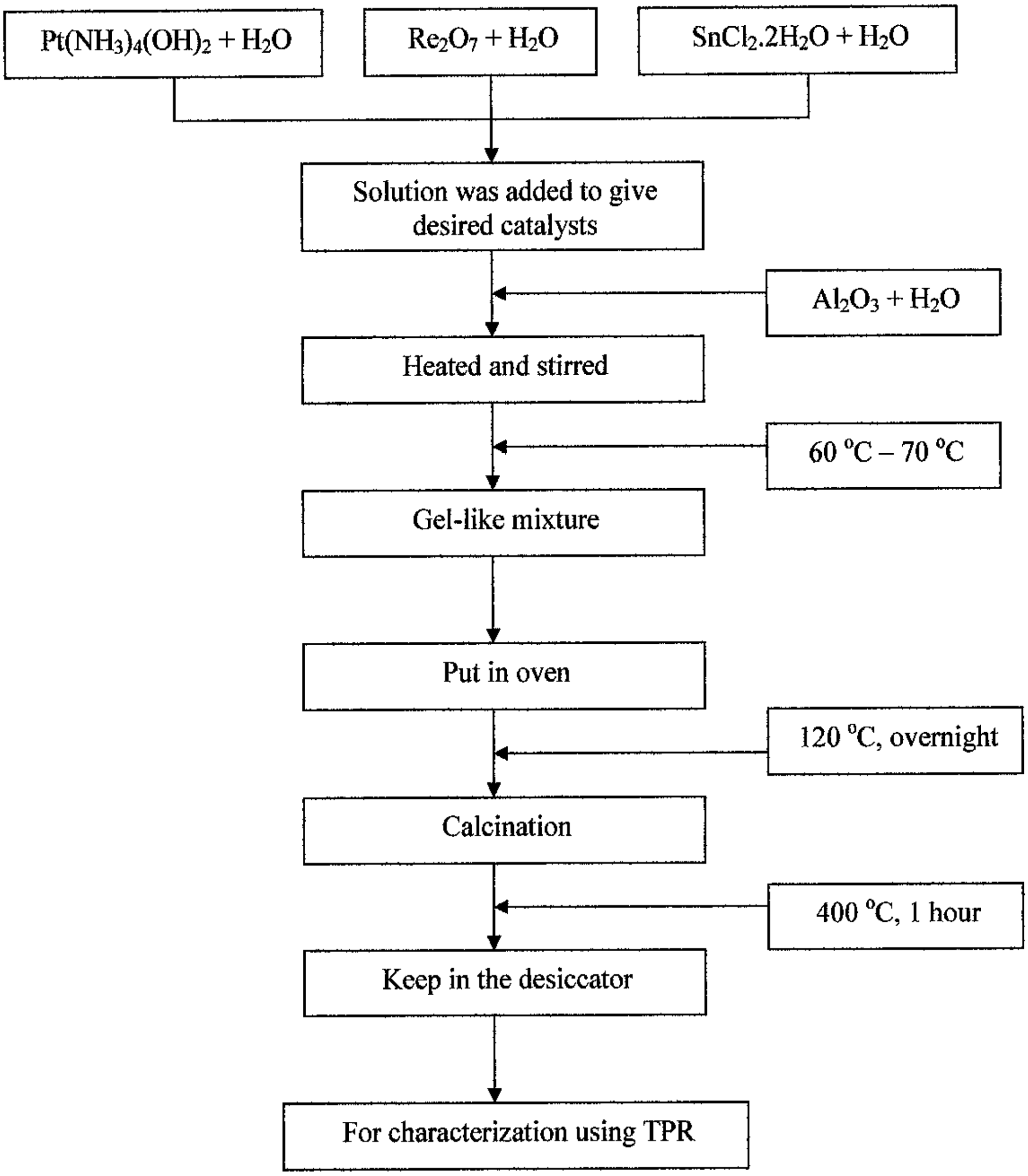


Figure 3.1: Simplified steps for preparing and pretreatment of Pt-Re-Sn/ Al_2O_3 catalyst

3.2 Catalyst Pretreatment

Extra treatment had been done to the sample catalysts by doing calcination. The steps for calcination had been done as below:

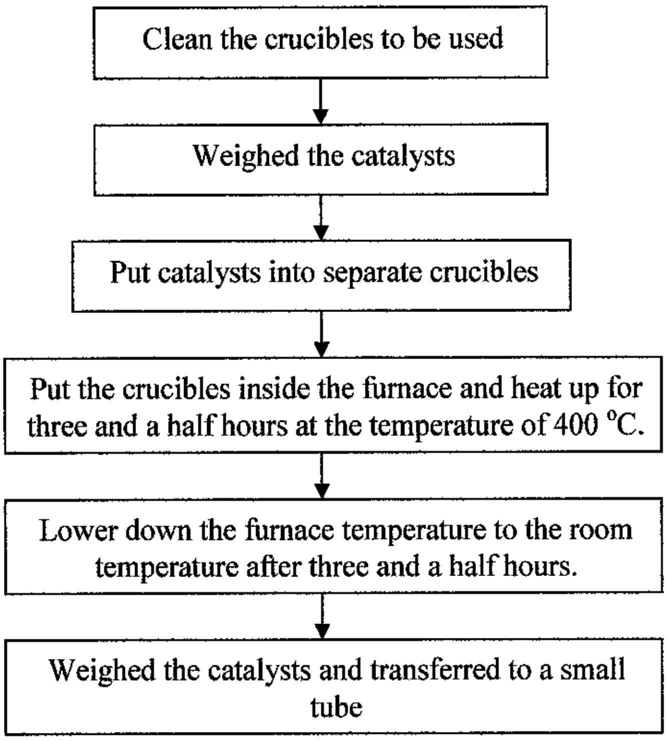


Figure 3.2: Simplified pretreatment steps for the catalysts

As a precaution, the furnace must be heated incrementally to avoid overheated. For example, the temperature is increased to 100 °C for the first one hour and then to 250 °C and finally until it reached 400 °C. This precaution is taken after experiencing the overheated problem in which the temperature of the furnace shot up to 480 °C at the end of the pretreatment because the temperature has been set at 400 °C at the beginning of the pretreatment.

3.3 Characterization of the Catalysts

Temperature Programmed Reduction

There is only one characterization method used to analyze the catalyst. The method used is the Temperature Programmed Reduction (TPR). The TPD/R/O equipment located in the Petrochemical's lab at Block 3, Chancellor Complex has been used to run the TPR experiment.

3.3.1 Temperature Programmed Reduction for the Al_2O_3 support

The reducibility of the Al_2O_3 support was investigated by a temperature programmed reduction (TPR). 0.0205 g of catalysts was placed on a quartz wool bed in an external quartz tube, positioned vertically in the oven. Temperature was measured by K – type thermocouple. The sample was heated to 800 °C at a rate of 10 °C/min in a 5.42% H_2/N_2 gas, flow at the rate of 20 cc/min. The hydrogen consumption for the reduction was monitored by a TCD. Another TPR has been done for the Al_2O_3 support that has been calcined at 400 °C for four and a half hours. An amount of 0.0961 g of the support has been used for the TPR analysis.

3.3.2 Temperature Programmed Reduction for Pt/Al_2O_3 Catalysts

The reducibility of the Al_2O_3 support was investigated by a temperature programmed reduction (TPR). 0.035 g of catalysts was placed on a quartz wool bed in an external quartz tube, positioned vertically in the oven. Temperature was measured by K – type thermocouple. The sample was heated to 800 °C at a rate of 10 °C/min in a 5.42% H_2/N_2 gas, flow at the rate of 20 cc/min. The hydrogen consumption for the reduction was monitored by a TCD. This procedure is repeated for a calcined Pt/Al_2O_3 catalyst with a weight of 0.0714 g.

Another TPR analysis has been done for the Pt/Al_2O_3 catalyst by using different procedure. An amount of 0.0667 g Pt/Al_2O_3 catalyst was heated from 40 °C to 250 °C at a rate of 5 °C/min in 5.42 % H_2/N_2 gas, flowing at a rate of 20 cc/min. At reaching 250 °C, the heating was hold for 30 minutes. After 30 minutes, the sample is heated up to 350 °C at the same heating rate and gas flow. The heating is again hold for 30 minutes before continue to increase the temperature to 450 °C, 550 °C and 650 °C with 30 minutes of holding in between. The simplified steps are showed in Figure 3.3:

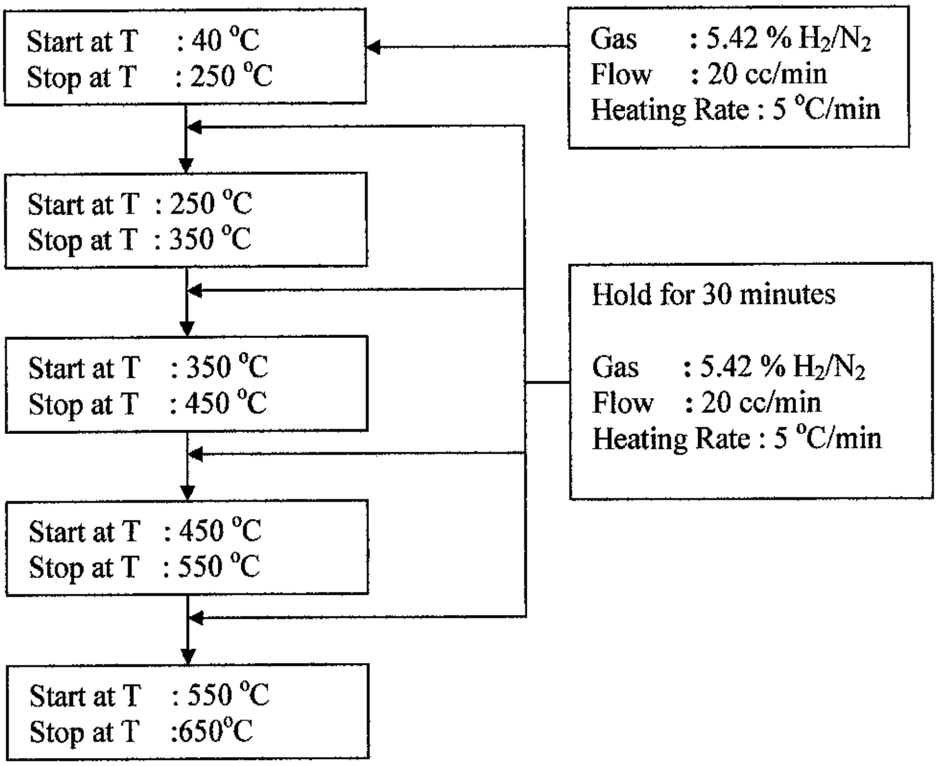


Figure 3.3: Simplified steps for TPR analysis

3.3.3 Temperature Programmed Reduction for Re/Al_2O_3 Catalysts

The reducibility of the Re/Al_2O_3 was investigated by a temperature programmed reduction (TPR). 0.0546 g of catalysts was placed on a quartz wool bed in an external quartz tube, positioned vertically in the oven. Temperature was measured by K – type thermocouple. The sample was heated to 800 °C at a rate of 10 °C/min in a 5.42% H_2/N_2 gas, flowing at the rate of 20 cc/min. The hydrogen consumption for the reduction was monitored by a TCD. This procedure is repeated for a calcined Re/Al_2O_3 catalyst with a weight of 0.0514 g.

3.3.4 Temperature Programmed Reduction for Sn/Al_2O_3 Catalysts

The reducibility of the Sn/Al_2O_3 was investigated by a temperature programmed reduction (TPR). 0.0686 g of catalysts was placed on a quartz wool bed in an external quartz tube, positioned vertically in the oven. Temperature was measured by K – type thermocouple. The sample was heated to 800 °C at a rate of 10 °C/min in a 5.42% H_2/N_2 gas that is flowing at the rate of 20 cc/min. The hydrogen consumption for the reduction was monitored by a TCD. This procedure is repeated for Re/Al_2O_3 catalysts that have been calcined for 4 and half hours at the temperature of 480 °C and 400 °C. The amounts of catalysts used for the experiment are 0.0614 g and 0.0857 g respectively.

3.3.5 Temperature Programmed Reduction for $Pt\text{-}Re/Al_2O_3$ Catalysts

The reducibility of the $Pt\text{-}Re/Al_2O_3$ was investigated by a temperature programmed reduction (TPR). 0.0881 g of the $Pt\text{-}Re/Al_2O_3$ catalysts was placed on a quartz wool bed in an external quartz tube, positioned vertically in the oven. The catalyst used had been calcined for 4 and half hours at the temperature of 480 °C. Temperature was measured by K – type thermocouple. The sample was heated to 800 °C at a rate of 10 °C/min in a 5.42% H_2/N_2 gas that is flowing at the rate of 20 cc/min. The hydrogen consumption for the reduction was monitored by a TCD. This procedure is repeated for 0.1003 g $Pt\text{-}Re/Al_2O_3$ catalysts that have been calcined for 4 and half hours at the temperature of 400 °C.

3.3.6 Temperature Programmed Reduction for $Pt\text{-}Sn/Al_2O_3$ Catalysts

The reducibility of the $Pt\text{-}Sn/Al_2O_3$ was investigated by a temperature programmed reduction (TPR). 0.0816 g of catalyst was placed on a quartz wool bed in an external quartz tube, positioned vertically in the oven. This catalyst had been calcined for 4 and half hours at the temperature of 400 °C. The temperature was measured by K – type thermocouple. The sample was heated to 800 °C at a rate of 10 °C/min in a 5.42% H_2/N_2 gas that is flowing at the rate of 20 cc/min. The hydrogen consumption for the reduction was monitored by a TCD.

3.3.7 Temperature Programmed Reduction for Re-Sn/Al_2O_3 Catalysts

The reducibility of the Re-Sn/Al_2O_3 was investigated by a temperature programmed reduction (TPR). 0.0906 g of catalyst was placed on a quartz wool bed in an external quartz tube, positioned vertically in the oven. The catalyst had been calcined for 4 and half hours at the temperature of 400 °C. The temperature was measured by K – type thermocouple. The sample was heated to 800 °C at a rate of 10 °C/min in a 5.42% H_2/N_2 gas that is flowing at the rate of 20 cc/min. The hydrogen consumption for the reduction was monitored by a TCD.

3.3.8 Temperature Programmed Reduction for Pt-Re-Sn/Al_2O_3 Catalysts

The reducibility of the Pt-Re-Sn/Al_2O_3 was investigated by a temperature programmed reduction (TPR). 0.1525 g of catalyst was placed on a quartz wool bed in an external quartz tube, positioned vertically in the oven. The catalyst had been calcined for 4 and half hours at the temperature of 400 °C. The temperature was measured by K – type thermocouple. The sample was heated to 800 °C at a rate of 10 °C/min in a 5.42% H_2/N_2 gas that is flowing at the rate of 20 cc/min. The hydrogen consumption for the reduction was monitored by a TCD.

CHAPTER 4

RESULTS

This section consists of the observation and results of the characterization of the catalysts by using the temperature programmed reduction (TPR). This study did not mention in detailed about the preparation methods of the monometallic catalysts (Pt/Al_2O_3, Re/Al_2O_3, Sn/Al_2O_3, bimetallic catalysts ($Pt\text{-}Re/Al_2O_3$, $Pt\text{-}Sn/Al_2O_3$, $Re\text{-}Sn/Al_2O_3$), tri-metallic catalysts ($Pt\text{-}Re\text{-}Sn/Al_2O_3$).and alumina support since the catalysts have been prepared earlier from the student in UPM.

4.1 Observations

The calcinations step had been done for few of the catalysts. Table 4.1, 4.2, 4.3 and 4.4 shows the observation of the colors change for the catalyst before and after the calcinations.

Table 4.1: Calcinations of Pt/Al_2O_3 and Re/Al_2O_3 (400°C)

Catalyst	**Before**	**After**
Pt/Al_2O_3	Light Grey	Dark Grey
Re/Al_2O_3	White	White

Table 4.1 shows the first set of catalysts that had been calcined; Pt/Al_2O_3 and Re/Al_2O_3. Both of these catalysts had been successfully calcined and the characterization results had gave a good temperature profile therefore no other calcinations are needed for these catalysts. These temperature profiles are being compared with the uncalcined temperature profiles in the next section.

Table 4.2: Calcinations of fresh Al_2O_3, Sn/Al_2O_3, $PtRe/Al_2O_3$, $PtSn/Al_2O_3$ and $ReSn/Al_2O_3$ (480°C)

Catalyst	**Before**	**After**
Fresh Al_2O_3	White	White
Sn/Al_2O_3	White	White
$PtRe/Al_2O_3$	Light Grey	Dark Grey
$PtSn/Al_2O_3$	Light Grey	Dark grey
$ReSn/Al_2O_3$	White	White

Table 4.2 shows the calcinations of few catalysts at a temperature at 480°C. Technically, this temperature is not the intended temperature for the calcinations, but the instability of the furnace had caused the temperature to shot up above 400°C. Due to this reason, the catalyst had been expected to be sintered due to extra heating and it has been proved by the result of the TPR in which no temperature profiles has been observed for $PtSn/Al_2O_3$, fresh Al_2O_3 and $ReSn/Al_2O_3$. Apart from that, the temperature profile for Sn/Al_2O_3 has deviated from the earlier temperature profile before calcinations.

Table 4.3: Calcinations of fresh Al_2O_3, Sn/Al_2O_3, $PtRe/Al_2O_3$, $PtSn/Al_2O_3$ and $ReSn/Al_2O_3$ (400°C)

Catalyst	**Before**	**After**
Fresh Al_2O_3	White	White
Sn/Al_2O_3	White	White
$PtRe/Al_2O_3$	Light grey	Dark grey
$PtSn/Al_2O_3$	Light grey	Dark grey
$ReSn/Al_2O_3$	White	Light Peach

Table 4.3 shows the observation for the second calcinations for the same set of catalysts. The procedure of heating up the furnace has been slightly modified to avoid the over heated condition of the furnace. The second calcinations shows the calcined catalysts still appear in the same color as the previous calcined catalysts, however, the rhenium-stanum catalyst had been found to appear slightly peach in color.

Table 4.4: Calcinations of Pt-Re-Sn/Al_2O_3 catalysts at (400°C)

Catalyst	**Before**	**After**
Pt-Re-Sn/Al_2O_3	Light grey	Dark grey

Table 4.4 shows the calcinations of the multimetallic catalysts, Pt-Re-Sn/Al_2O_3 at 400°C where the color changed from light grey to dark grey after the calcinations.

4.2 Temperature Profiles

4.2.1 TPR of Fresh Al_2O_3

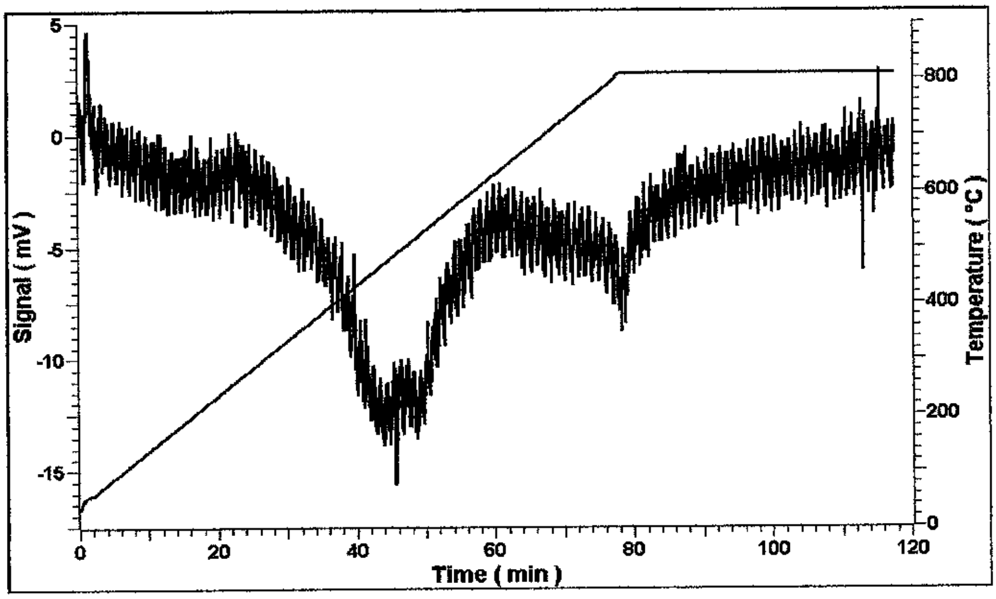


Figure 4.1: Temperature profile of Fresh Al_2O_3 before calcination

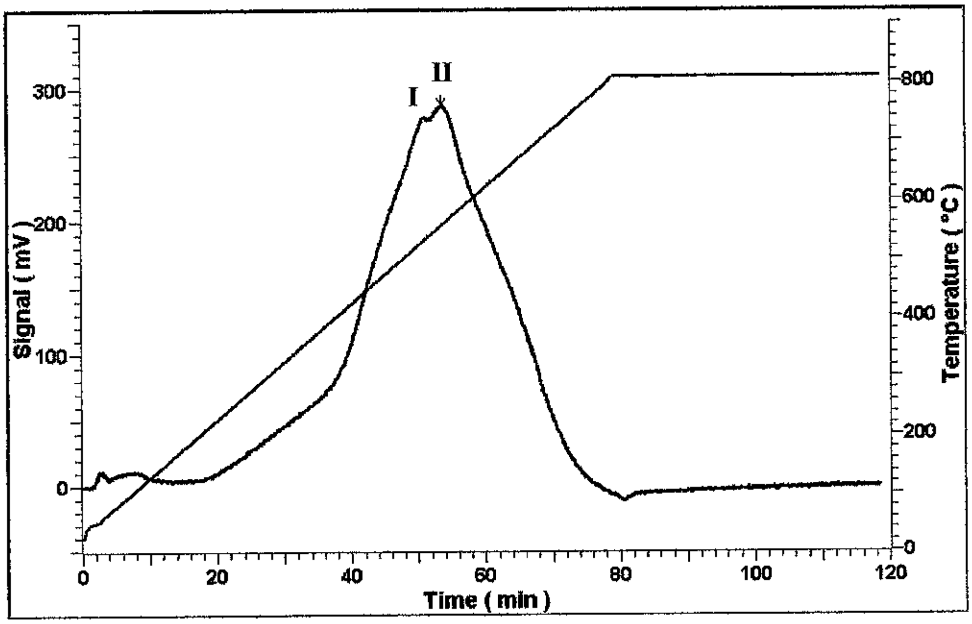


Figure 4.2: Temperature profile of Fresh Al_2O_3 after calcination at 400^oC

4.2.2 TPR of Pt/Al_2O_3

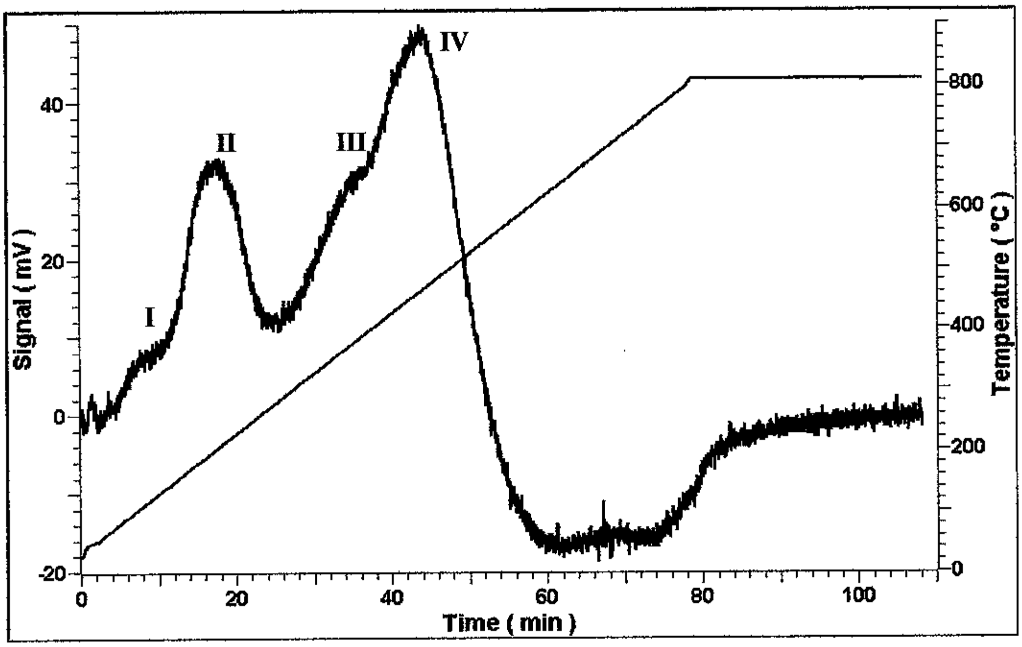


Figure 4.3: Temperature profile of Pt/Al_2O_3 before calcination

TPR for Pt/Al_2O_3 by sections of temperature range:

a) TPR of ***Pt/Al_2O_3*** (*25°C-250°*C)

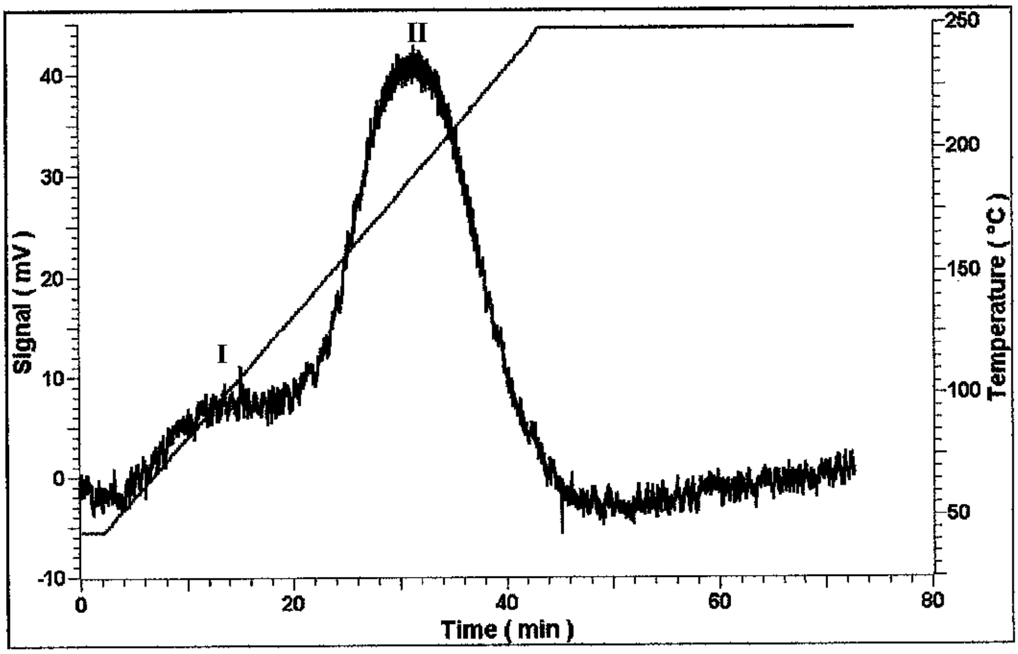


Figure 4.4: Temperature profile of Pt/Al_2O_3 before calcination (25°C-250°C)

b) TPR of ***Pt/Al_2O_3*** *(250°C-350°C)*

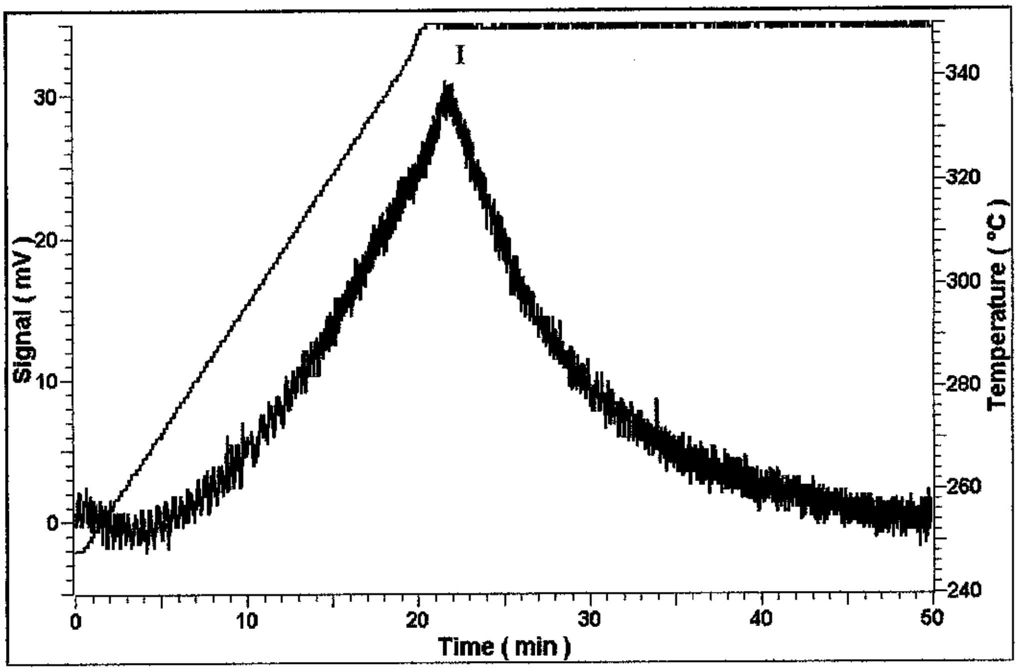


***Figure 4.5**: Temperature profile of Pt/Al_2O_3 before calcination (250°C-350°C)*

c) TPR of ***Pt/Al_2O_3*** *(350°C-450°C)*

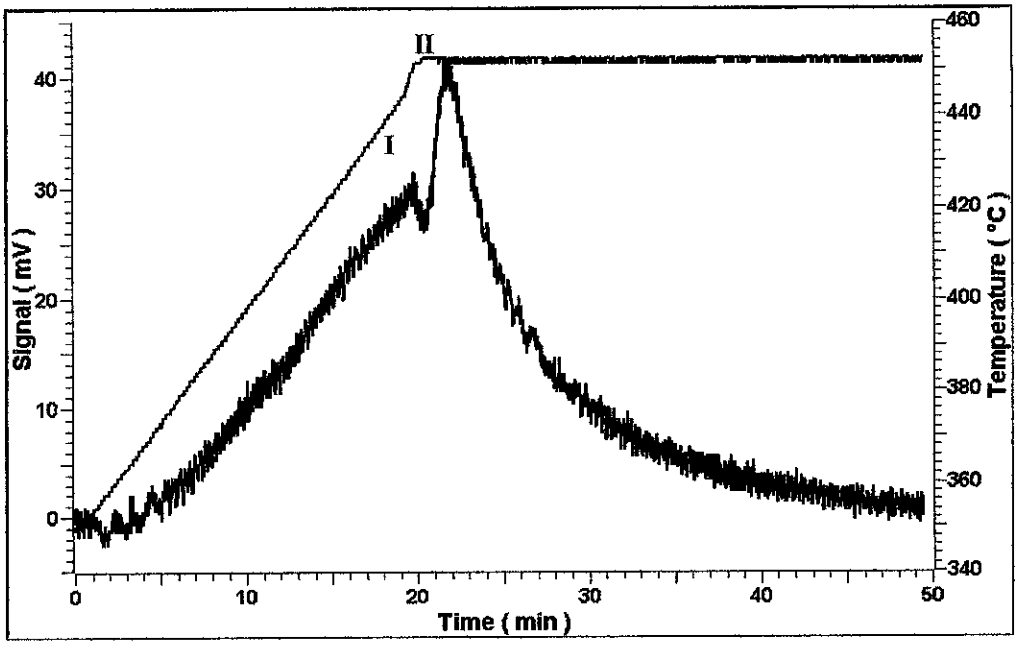


***Figure 4.6**: Temperature profile of Pt/ Al_2O_3 before calcination (350°C-450°C)*

d) *TPR of* ***Pt/*****Al_2O_3** *(450°C - 550°C)*

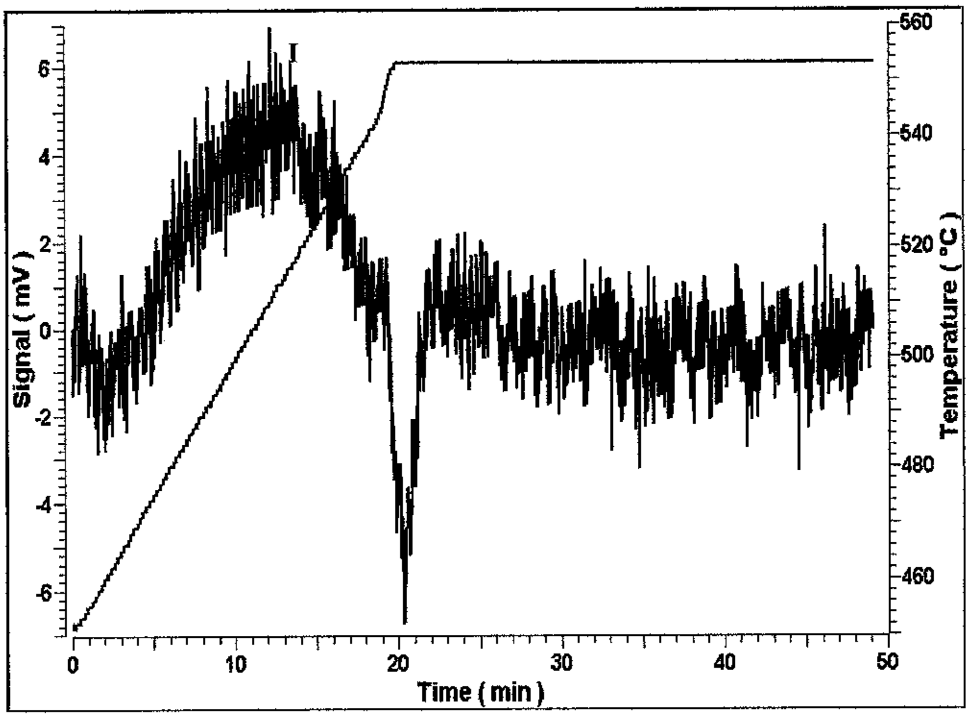


***Figure 4.7**: Temperature profile of Pt/ Al_2O_3 before calcination (450°C - 550°C)*

e) *TPR of* ***Pt/*****Al_2O_3** *(550°C - 650°C)*

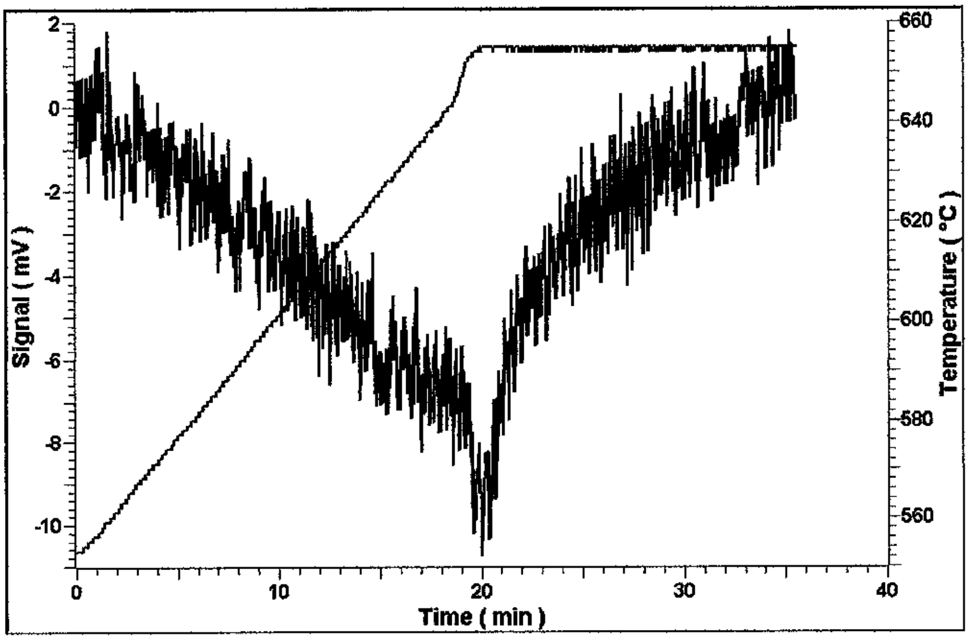


***Figure 4.8**: Temperature profile of Pt/ Al_2O_3 before calcination (550°C - 650°C)*

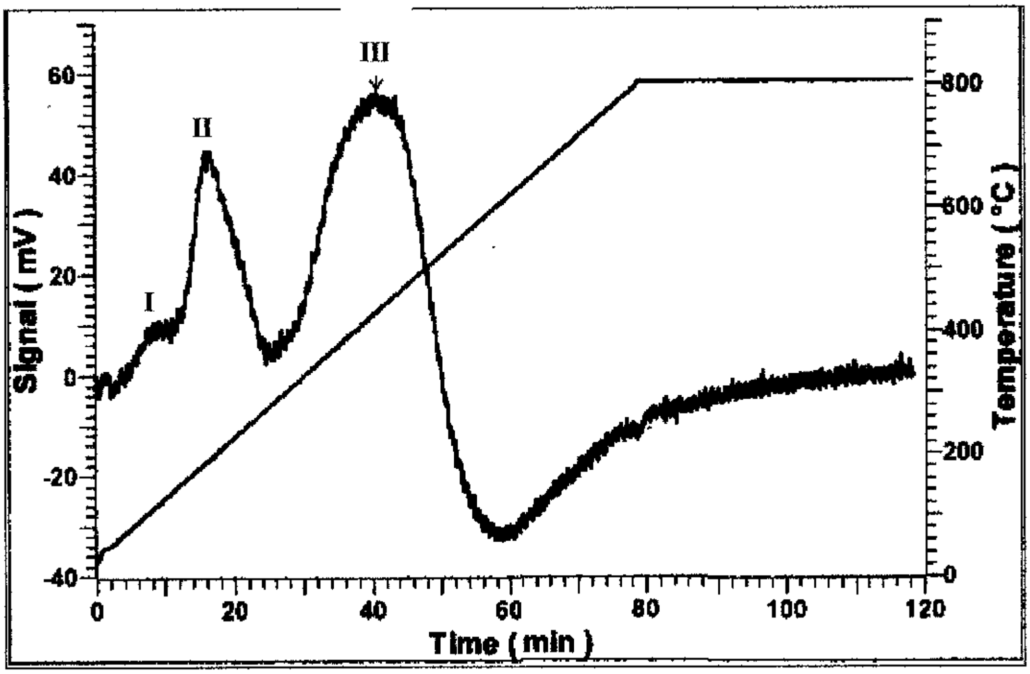


Figure 4.9: Temperature profile of Pt/ Al_2O_3 after calcination at 400°C

4.2.3 TPR of Re/Al_2O_3

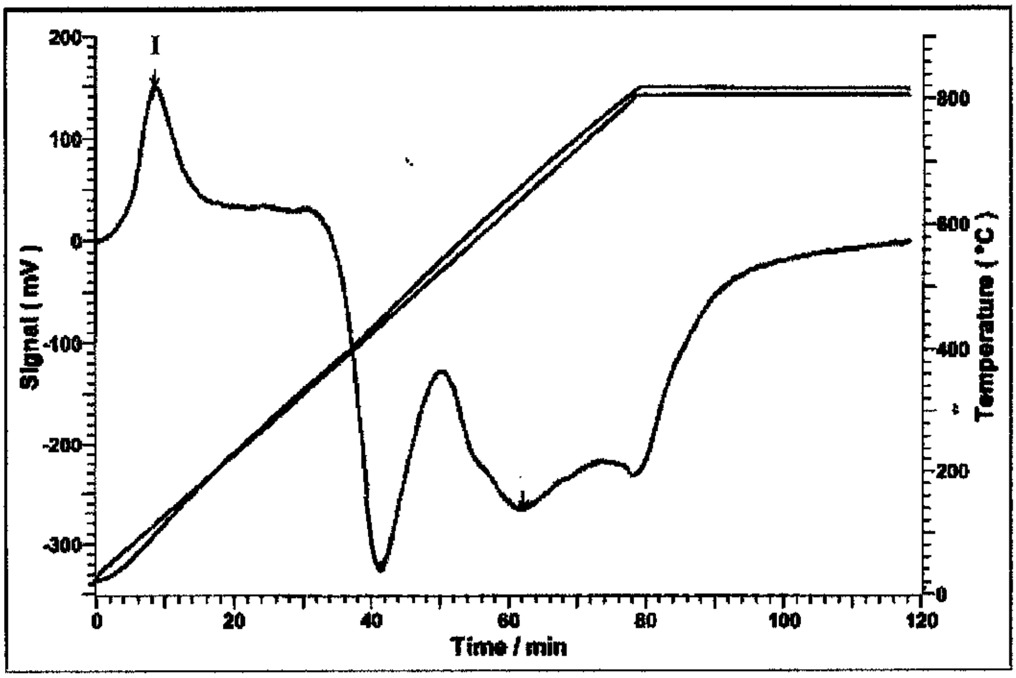


Figure 4.10: Temperature profile of Re/Al_2O_3 before calcination

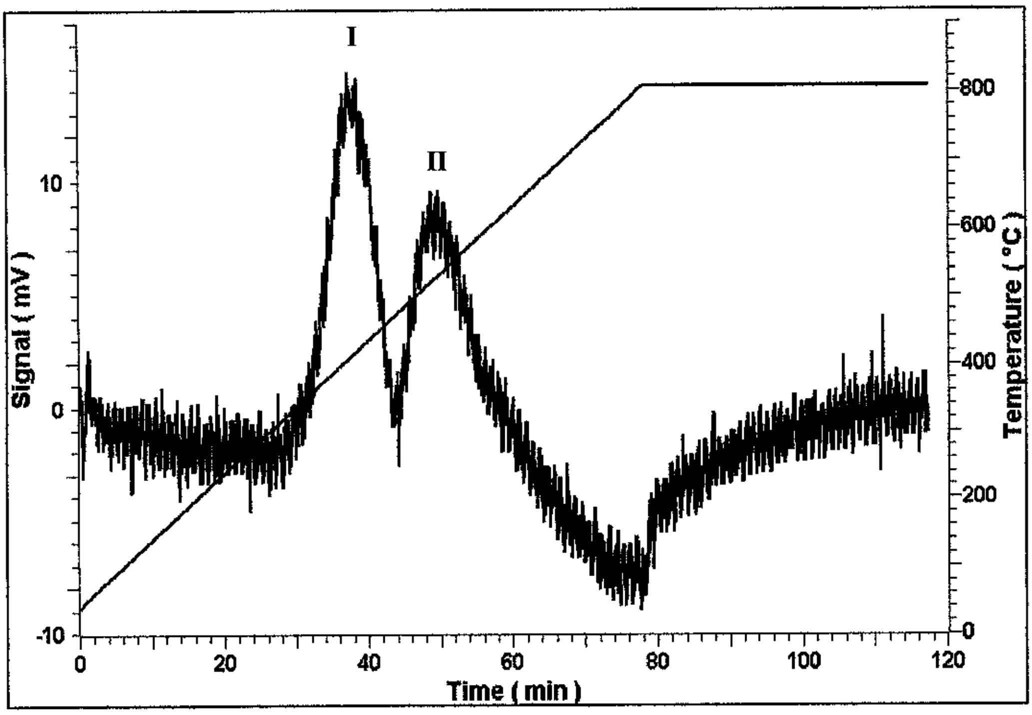


Figure 4.11: Temperature profile of Re/Al_2O_3 after calcination at 400 °C

4.3.6 TPR of Sn/Al_2O_3

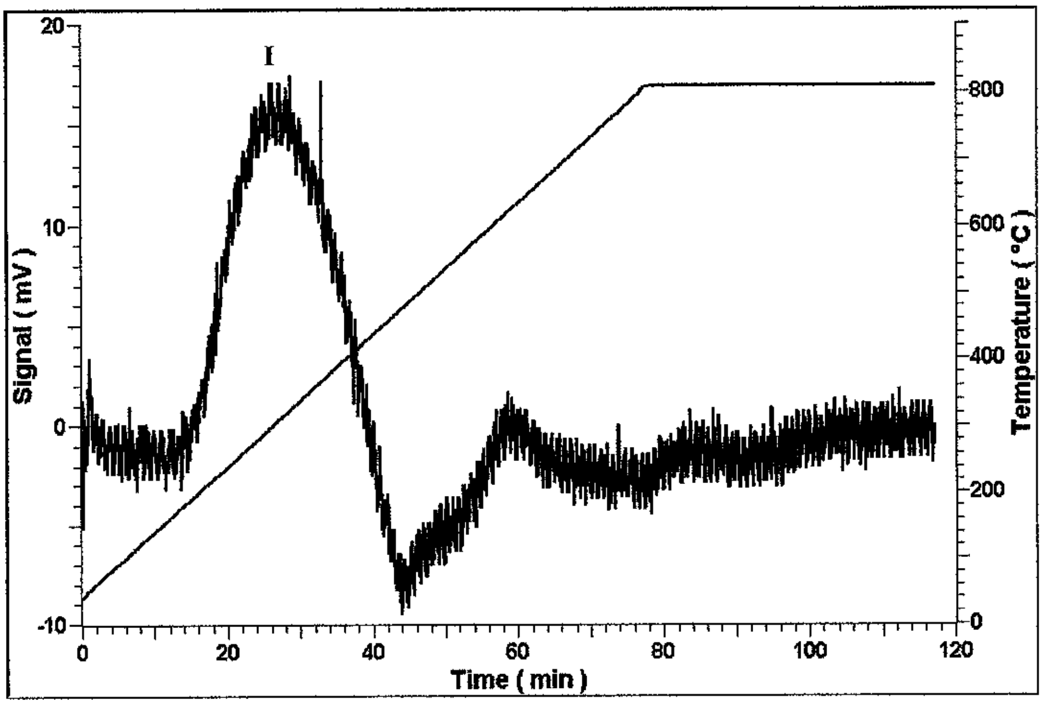


Figure 4.12: Temperature profile of Sn/Al_2O_3 before calcination

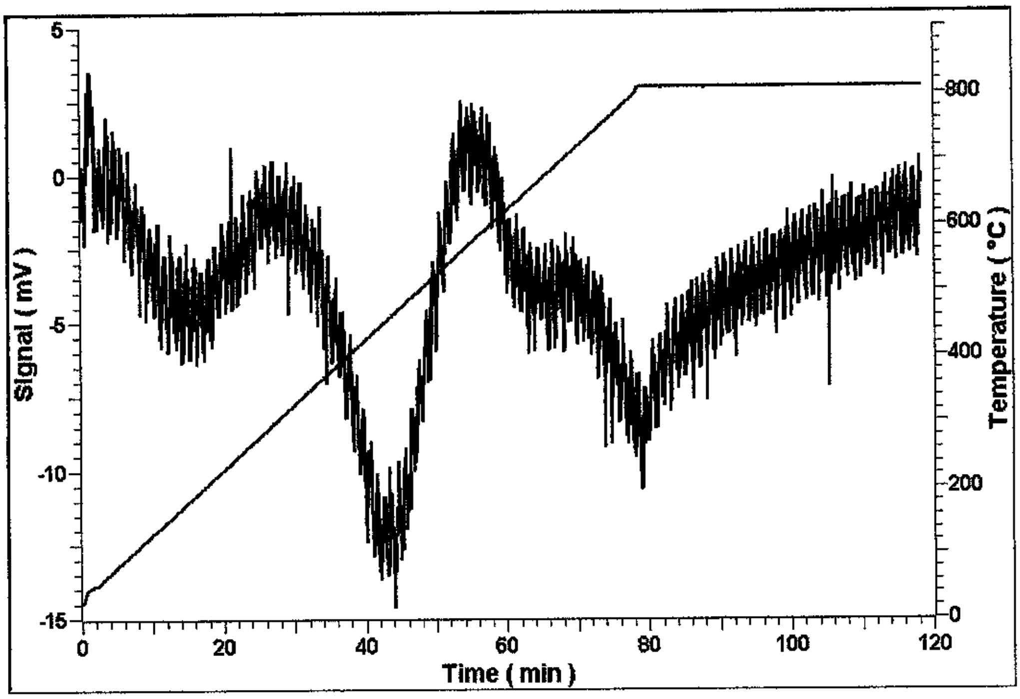


Figure 4.13: Temperature profile of Sn/Al$_2$O$_3$ after calcination at 480 °C

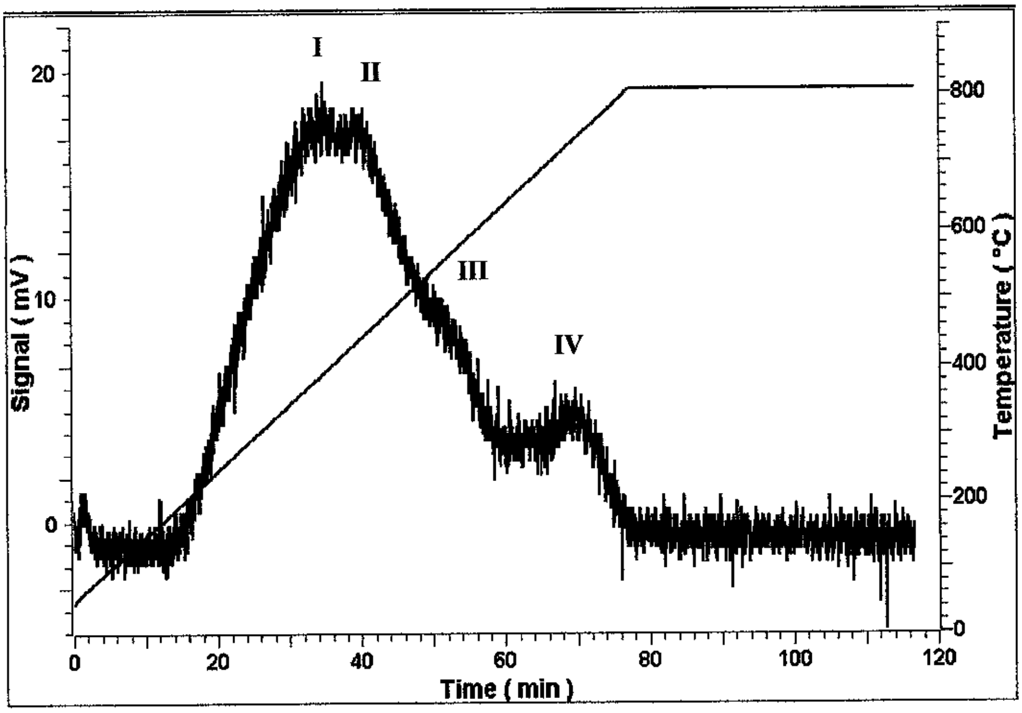


Figure 4.14: Temperature profiles of Sn/Al$_2$O$_3$ after calcination at 400 °C

4.2.5 TPR of Pt-Re/Al_2O_3

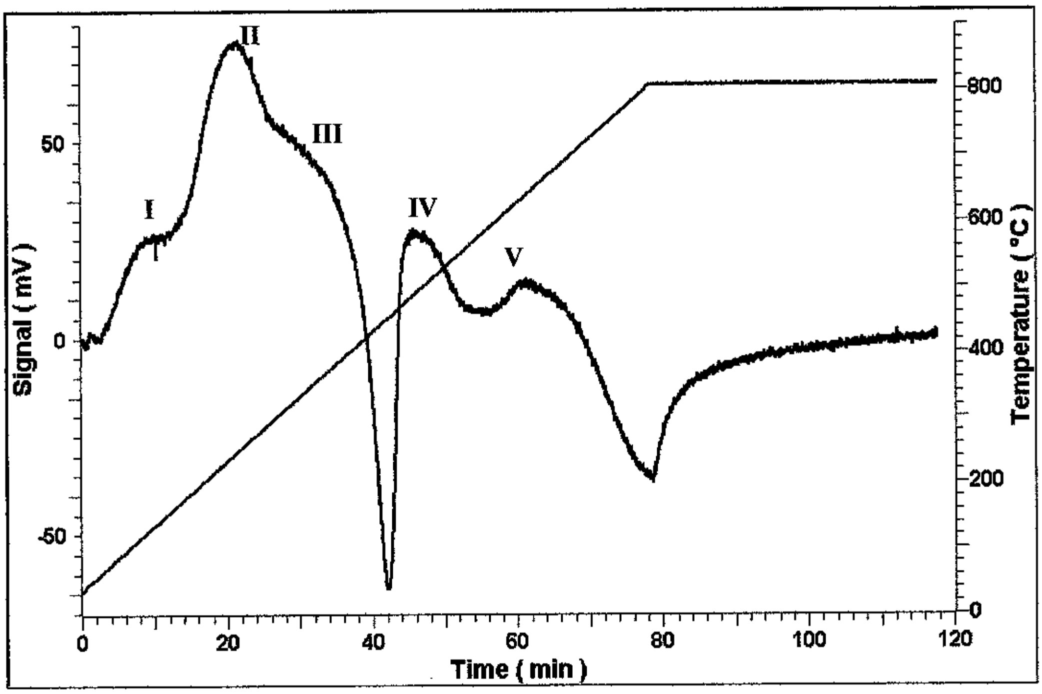


Figure 4.15: Temperature profiles of Pt-Re/Al_2O_3 after calcination at 480°C

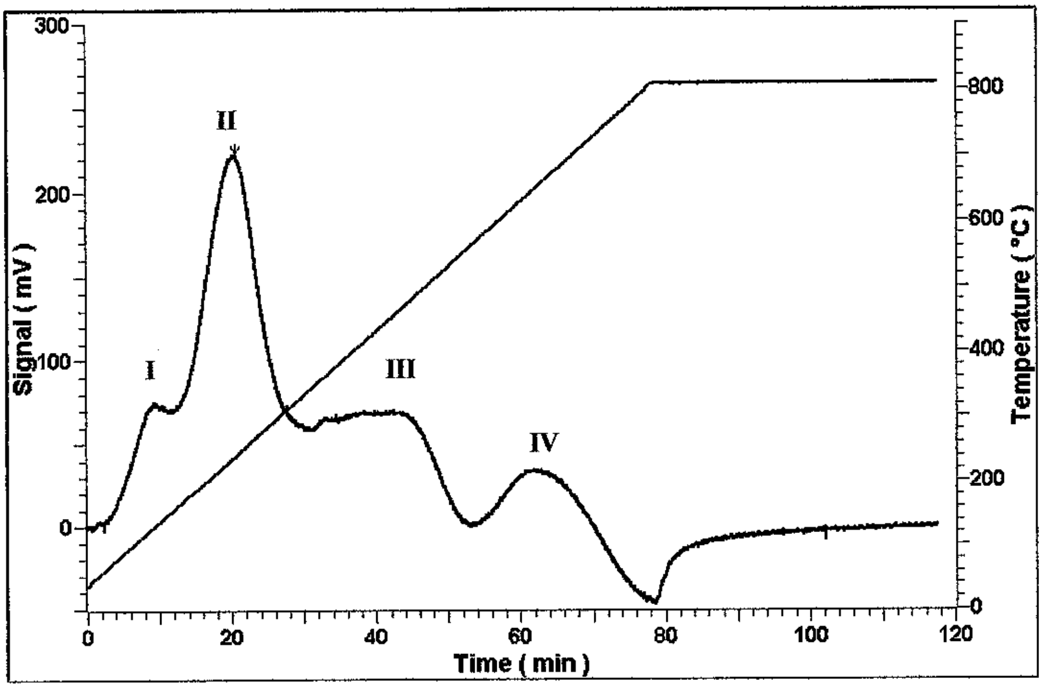


Figure 4.16: Temperature profile of Pt-Re/Al_2O_3 after calcination at 400 °C

4.2.6 TPR of Pt-Sn/Al_2O_3

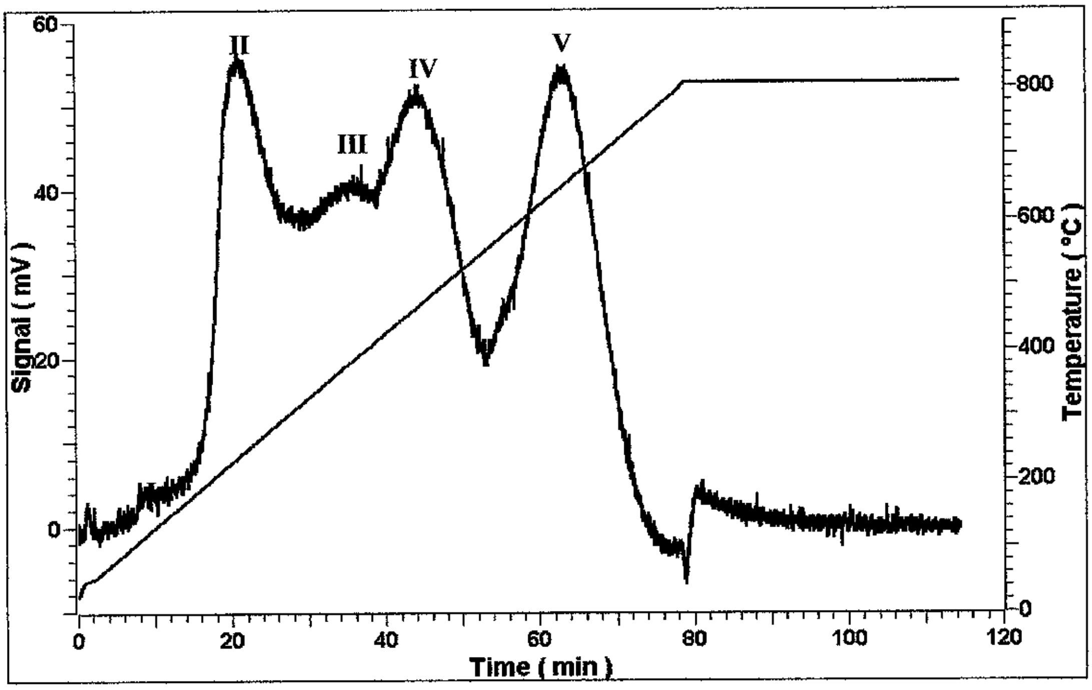


Figure 4.17: Temperature profile of Pt-Re/Al_2O_3 after calcination at 400 °C

4.2.7 Re-Sn/Al_2O_3

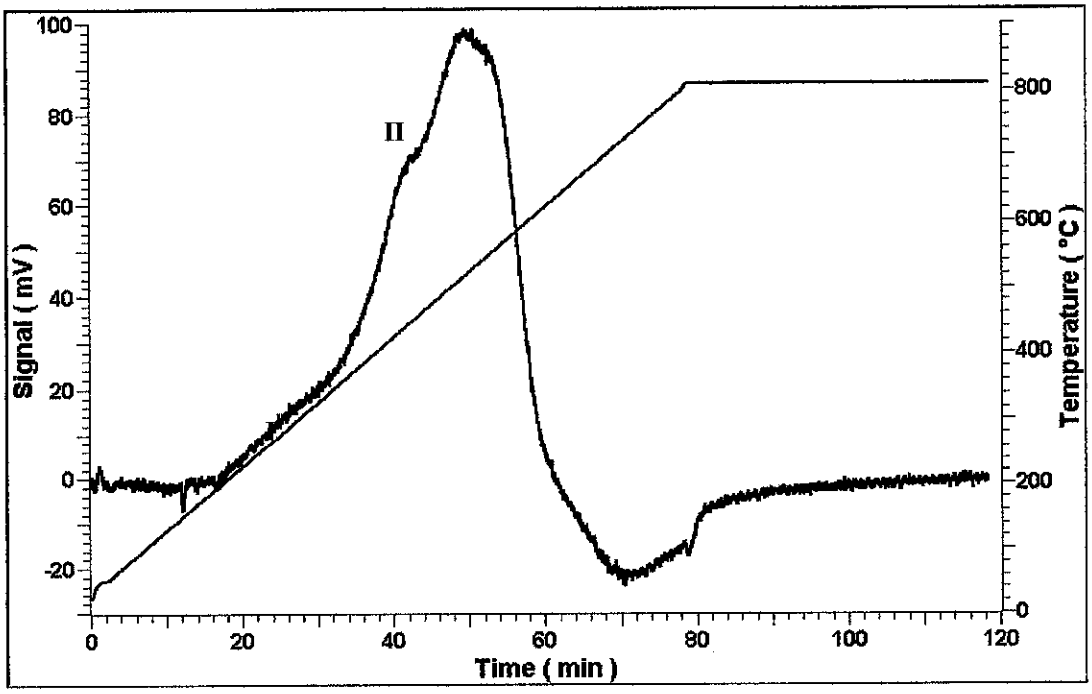


Figure 4.18: Temperature profile of Re-Sn/Al_2O_3 after calcination at 400 °C

4.2.7 Pt-Re-Sn/Al_2O_3

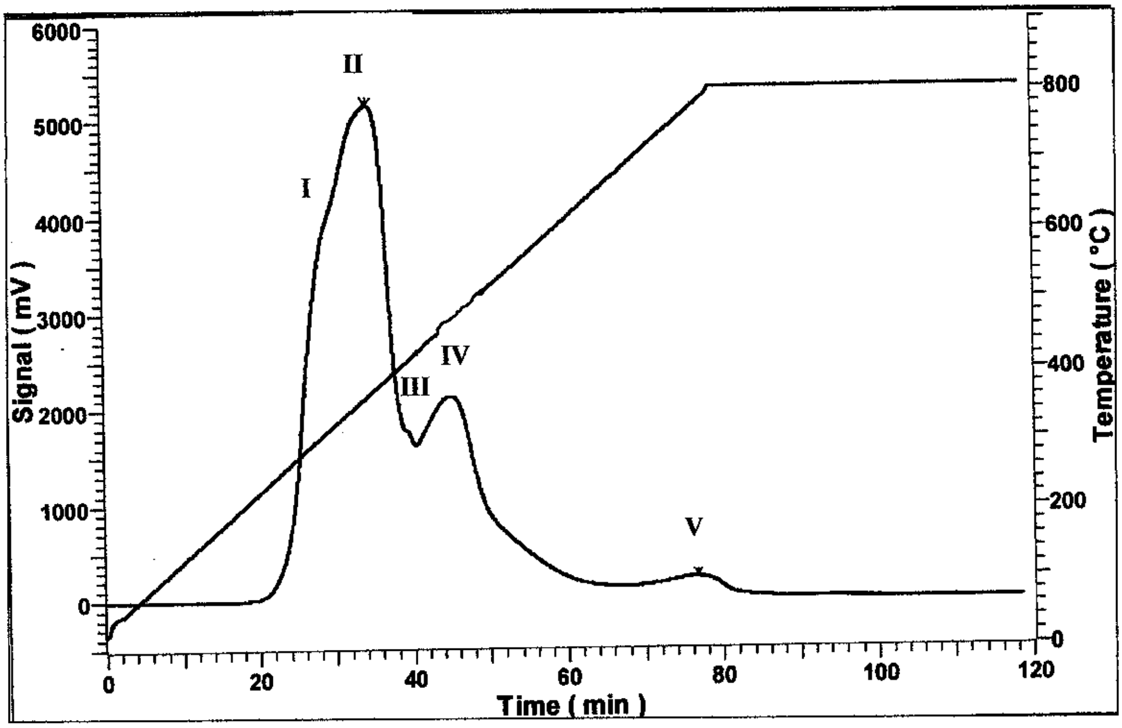


Figure 4.19: *Temperature profile of Pt-Re-Sn/Al_2O_3 after calcination at 400 °C*

4.3 Reduction Temperatures

The reduction temperature for all the catalysts had been summarized in Table 4.5:

***Table 4.5**: Reduction Temperatures of Catalysts*

Catalysts	**Temperature Programmed Reduction (TPR)**			
	Before Calcination		**After Calcination**	
			At 480°C	**At 400 °C**
Fresh Al_2O_3	NA		Peak I = 480 °C Peak II = 520 °C	
Pt/Al_2O_3	Peak I =100 °C Peak II = 180 °C Peak III = 360 °C Peak IV = 425 °C	i. 250 °C – 350 °C Peak I = 100 °C Peak II = 190 °C ii. 350 °C – 450 °C Peak 1= 350 °C iii. 350 °C – 450 °C Peak 1 = 420 °C Peak II = 442 °C iv. 450 °C – 550 °C Peak I = 510 °C		Peak I = 100 °C Peak II = 180 °C Peak III = 420 °C

Table 4.5: *Reduction Temperatures of Catalysts*

Catalysts	**Temperature Programmed Reduction (TPR)**		
	Before Calcination	**After Calcination**	
		At 480°C	**At 400 °C**
Re/Al$_2$O$_3$	NA		Peak I = 400 °C Peak II = 520 °C
Sn/Al$_2$O$_3$	Peak I = 340 °C	NA	Peak 1 = 380 °C Peak II = 425 °C Peak III = 520 °C Peak IV = 720 °C
Pt-Re/Al$_2$O$_3$	-	Peak I = 140 °C Peak II = 287 °C Peak III = 378 °C Peak IV = 486 °C Peak V = 640 °C	Peak I = 120 °C Peak II = 220 °C Peak III = 340 °C Peak IV = 460 °C Peak V = 640 °C

***Table 4.5**: Reduction Temperatures of Catalysts*

Catalysts	Temperature Programmed Reduction (TPR)		
	Before Calcination	After Calcination	
		At 480°C	At 400 °C
Pt-Sn/Al$_2$O$_3$	-	Peak I = 120 °C Peak II = 250 °C Peak II = 400 °C Peak III = 460 °C Peak IV = 660 °C -	
Re-Sn/Al$_2$O$_3$	-	-	Peak I = 260 °C Peak II = 440 °C Peak II = 490 °C Peak IV = 520 °C
Pt-Re-Sn/Al$_2$O$_3$	-	-	Peak I = 260 °C Peak II = 320 °C Peak II = 340 °C Peak IV = 410 °C Peak V = 800 °C

CHAPTER 5

DISCUSSION

There are eight samples being characterized in this experiment, consists of the support itself (γ-Al_2O_3), the supported monometallic catalyst of the noble materials (Pt/ Al_2O_3, Re/Al_2O_3 and Sn/Al_2O_3), the supported bimetallic catalysts (Pt-Re/Al_2O_3, Pt-Sn/Al_2O_3 and Re-Sn/Al_2O_3) and the supported tri-metallic catalysts(Pt-Re-Sn/Al_2O_3). The TPR technique allows to get information about the interaction of the metal components by means of the measurement of the hydrogen consumption during the reduction of the oxides at a constant heating. The temperature at which reduction occurs and the number of reduction peaks depend on the oxidation state of the metals, the interaction of the oxides among them and with the support and on the possible catalytic action of Pt or other elements present or generated during reduction. Eventually, the reduction temperature represent the temperature at which the hydrogen is energized enough to be converted into water vapor. The characterized samples are discussed in this section based on the results obtained from the experiment.

5.1 Support

*TPR of **Fresh** Al_2O_3*

The temperature profiles for this support are shown on Figure 4.1 and 4.2. Figure 4.1 shows the temperature profile of the support before calcination and no peak has been detected in this profile. The calcinations of the support for four and half hours at the temperature of 400 °C gave a temperature profile as shown on Figure 4.2 whereby two peaks has been detected at the temperatures of 480 °C and 550 °C.

5.2 Supported Monometallic Catalysts

5.2.1 TPR of Pt/Al_2O_3

TPR of Platinum has been done for few times and the thermograms are shown from Figure 4.3 to Figure 4.9. Temperature profile shown in Figure 4.3 does not give a good result and therefore, a second TPR characterization had been done. This figure shows a temperature profiles with 4 peaks whereby the peaks are identified with roman numbers on all the profiles. The first peak is detected at temperature of 100°C and followed by the second peak at 180°C, third peak at 360°C ad the last peak is at 425°C. This results does not follow the results of TPR obtained by McNicol, Blanchard and Yao on Alumina-supported Platinum where there is only one reduction peak found approximately at 280°C where the loading for the catalysts used are <1 wt% and different platinum salts had been used for the catalysts preparation. Jones (1986) had presented the conclusion made by McNicol about the single reduction temperature that since this temperature are so far above the reduction temperature of the tetravalent platinum chlorides and oxides, therefore there must be an interaction between the platinum species and the γ- Al_2O_3 surfaces.

Jones had also shown the TPR carried out by McNicol on a wide range of platinum compounds of importance preparation, e.g. $PtCl_4$, H_2PtCl_6, $Pt(NH_3)_2(NO_2)_2$, $Pt(NH_3)_4(OH_2)$, $H_2Pt(OH)_6$. The platinum salts that had been used during the catalysts preparation is $Pt(NH_3)_4(OH_2)$, and the TPR profiles found of the catalysts displayed four peaks. These results correspond to the TPR of the alumina-supported platinum in this experiment. They had also noted that the Cl^- containing salts are significantly more difficult to reduce than the OH^- salts. The reduction peaks given by McNicol were on the range of 150°C to 217°C. This reduction temperature might correspond to the first and second peaks displayed in Figure 4.4, Figure 4.5, Figure 4.6 and Figure 4.9 where the reduction temperatures are at 100 °C and 180°C. The third and fourth peak in Figure 4.4 and the third peak in Figure 4.9 correspond to the reduction temperature of the supports.

Jones had also presented TPR done by Huzinga for 5 wt% Pt on Al_2O_3 which has been prepared from a compound that did not contain Cl. It was found that that the main reduction took place at 473 K or equivalent to 200°C and as the temperature of calcinations increases, the TPR peak moves to lower temperature and oxidation state of Pt to higher values.

5.2.2 TPR of Re/Al_2O_3

Rhenium is a second component that to platinum in catalytic reforming catalysts. The salt precursor Re_2O_7 had been used to prepare the γ-Al_2O_3 supported catalyst. There were three TPR that has been carried out for the Rhenium/Al_2O_3 and the temperature profiles are shown in Figure 4.10, Figure 4.11 and Figure 4.12. The first figure (Figure 4.10) shows a temperature profile with a significant negative peak towards the end of the TPR.

The second TPR plot (Figure 4.11) shows one reduction peak at 100 °C that signifies a hydrogen uptake. However, based on the literature review, there is no evidence of Rhenium being reduced at this temperature. Therefore, it cannot be concluded this temperature is the reduction temperature of Rhenium. Apart from this positive peak, there are three more negative peaks observed from the figure. A negative peak might indicate the release of hydrogen or any other substance that have similar conductivity with the hydrogen. Nevertheless, the composition cannot be determined unless a mass spectrometer is used in order to check the composition of the gas being detected by the TCD.

The third TPR plot shows a temperature profile with two reduction peaks that has been detected at 400 °C and 520 °C. Jones (1986) has reported that the work done by Bolivar (1975), Webb (1975) and McNicol (1977) had shown that the rhenium supported on γ- Al_2O_3 is completely reduced to zero valent state by hydrogen at temperature ranging from 400 °C to 550 °C. Since the temperature profiles obtained gave two reduction peaks that are similar to that of Bolivar, Webb and McNicol, hence it can be assumed that the Rhenium is reduced to zero valent state during the experiment. However, another TPR study on Rhenium/Al_2O_3 by Johnson and LeRoy [56] gave a different claimed where the Rhenium supported on Alumina is reported to be reduced exclusively to Re^{4+}. Nevertheless, Jones had concluded that the discrepancies of these two results are due to the different conditions of preparation and reduction of catalysts involved.

It should be noted that the rhenium sample used in the third TPR was calcined for 4 hours and a half at the temperature of 400 °C in a furnace and the calcinations step could had affected the reduction temperature. Jones (1986, pg.140) had suggested that the calcinations steps might had a role of fixing the rhenium compound to the γ- Al_2O_3 in some kind of compound formation such that upon subsequent reaction at high temperatures a good dispersion of rhenium is obtained.

5.2.3 TPR of Sn/Al_2O_3

Tin or Stanum are used in the form of catalysts and catalysts supports in CO oxidation and as a component in reforming catalysts for increasing the octane rating of petrol. It can also act as a promoter of platinum in the electrocatalytic oxidation of methanol. The $SnCl_2.2H_2O$ salt had been used in preparing the Stanum/Al_2O_3 sample.

Overall, there were three TPR that has been done for this sample. Figure 4.13 shows the first TPR where hydrogen consumption had been observed at the temperature of 320 °C. This temperature indicates that only one Tin species has been reduced. The second TPR which is displayed in Figure 4.14 shows negligible hydrogen consumption at the temperature of 580°C. Nevertheless, the third TPR has given a totally different temperature profile compared to the first two TPR. No negative peaks have been observed and there are four reduction temperatures has been detected in the profile. The maximum reduction temperatures occurred at the temperature of 380 °C and 425 °C. A small shoulder is detected at the temperature of 560 °C and 720 °C.

These temperatures profiles are quite similar with the TPR done by Silvia, Santos, Mandes, Jordan and Fraga (2003, pg. 157 -158). Their TPR of calcined Stanum/Al_2O_3 yield two broad reduction peaks with maxima at ~320 and ~510 °C, respectively, and a shoulder at ~680 °C. Their results had been compared to the TPR done by Volter and Lieske (1984). Volter and Lieske reported that after calcination at 500 °C, the oxidized tin was present on alumina in two different species: a strongly stabilized oxide that reduced at 520–550 °C by formation of a Sn(II)–alumina surface complex; a less stabilized dispersed oxide that reduced at 280–350 °C leading to Sn(II) and metallic tin.

Carvalho, Pieck, Rangel, Figoli, Grau, Reyer and Parera (2004) obtained a TPR plot of Sn oxide with broad temperature range, starting at 150 °C and ending at 550 °C, with two main reduction regions in the 200–300 and 380–520 °C ranges. They suggested that this is an indication of a heterogeneous interaction of Sn oxide with alumina, interaction that is able to produce tin aluminates. Their literature review revealed that Sn(IV) is reduced to Sn(II) which, due to the strong interaction with the support, is not reduced to Sn^0.

The occurrence of the fourth reduction peak at 720 °C in this experiment however is suggested to be the reduction of the aluminates. Alonso, Jorge and Santos in their work had obtained a TPR profile with two large reductions at 450 °C and small intensity at 940 °C. They concluded that the second reduction temperature is the reduction of the aluminates.

5.3 Supported Bimetallic Catalysts

5.3.1 TPR of Pt-Re/Al_2O_3

Platinum/rhenium bimetallic catalysts supported on γ- Al_2O_3 are used in the modern catalytic reforming process where they display better activity, selectivity, and stability than the monometallic platinum catalyst. Jones had mentioned that increase in performance are believed to be resulted from the alloying between platinum and rhenium though only small metal amounts are present in the catalysts there so finely dispersed that alloying cannot be identified straight (1986, pg.161)

Figure 4.16 displayed the first TPR of this catalyst where it had been calcined for four and a half hours at the temperature of 480 °C prior to characterization. The temperature profiles show five reduction peaks with a sharp falling occurred at the temperature of 440 °C. The first and second peaks occurred at 140°C and 287 °C which are similar to the reduction temperature of the monometallic platinum catalyst. However, this reduction temperature had been dislocated to a higher temperature maybe due to the interaction between platinum and rhenium which makes it's more difficult to be reduced. The other two peaks that occurred at the temperature of 378 °C and 486 °C gave similar reduction peaks to the study done by Pieck, Gonzalez and Parera (2001, pg. 309).

Pieck, Gonzalez and Parera explained that the location of reduction peaks for Pt-Re/Al_2O_3 catalysts depends on the degree of interaction between Pt and Re. They had done a TPR study for a Pt-Re/Al_2O_3 catalyst prepared by catalytic reduction and activated using both activation procedures (calcination–reduction or direct reduction) to investigate the influence of the type of activation method.

Their finding shows that the catalyst activated by calcination–reduction, with a moderate degree of Pt-Re interaction as pointed out before, has two reduction peaks. The first peak at 350°C is due to reduction of Pt and part of Re oxides. The second peak at about 500°C corresponds to the reduction of segregated Re oxide. PtO_2 is reduced to Pt^0 which catalyzes the reduction of Re_2O_7 at a lower temperature than that found for Re alone. The peak at 500°C corresponds to the reduction of Re_2O_7 located so far from Pt that its catalytic effect is not possible. The direct-reduction method resulted in the first reduction peak at 350°C is greater, than in the sample calcined-reduced. This peak is due to the co-reduction of Pt and Re and shows the higher degree of Pt-Re interaction. On the other hand, the second reduction peak is smaller and occurs at higher temperatures for this catalyst. (2001, pg.309).

Temperature profile for the second TPR is shown on Figure 4.17. This temperature profile shows five reduction peak with the main consumption occurred at 220 °C. The main reduction at 220 °C and the small shoulder that appear at 140°C is assumed to be the reduction of the PtO because the reduction temperature is similar to the reduction of the monometallic. The reduction peak at the temperature of 340 °C correspond to the the reduction of Pt and part of Re oxides meanwhile at 460 °C is the reduction of Re_2O_7 that located so far from Pt. The fifth peaks that occurred at 640 °C in Figure 4.16 and 4.17 might be due to the reduction of the support.

5.3.2 TPR of Pt-Sn/Al_2O_3

The TPR plot of Pt–Sn in Figure 4.17 shows five peaks with major reduction occurs at the temperature of 250 °C, 460 °C and 660 °C. It has been observed that the profile of this bimetallic catalyst does not match the sum of the profiles of the monometallic catalysts Pt and Sn as agreed by Dautzenberg et. al (1980) and Larsson (1997). Larsson (1997) has concluded that some of the tin in the Pt-Sn catalyst must have been reduced at a lower temperature than in the Sn catalyst which is most probably caused by platinum catalyzing the reduction of the tin. The plot shows that the peaks at 380 °C, 425 °C, 520 °C and 720 °C in Sn/Al_2O_3 catalysts have been shifted to 250 °C, 400 °C, 460 °C and 660 °C respectively for the Pt-Sn/Al_2O_3 catalyst. A small shoulder that appears at the temperature of 120 °C could be the reduction of the Platinum Oxide metal.

Carvalho et. al (2004, pg.8) explained that the reduction of Sn oxide that occurs in the range of 380–520 °C of monometallic Sn, in Pt–Sn occurs at lower temperature due to the catalytic action of Pt. Sn(IV) is reduced to Sn(II) and in the neighbourhood of Pt a small part of Sn(II) is reduced to Sn^0 which is alloyed to Pt. He also concluded that the additional hydrogen consumption in the bimetallics compared to Pt is greater in Pt–Re than in Pt–Sn because most part of Re(VII) is reduced to Re(0) while Sn(IV) is mostly reduced to Sn(II) and a small fraction up to Sn(0).

5.3.3 TPR of Re-Sn/Al_2O_3

The TPR diagram of bimetallic Re–Sn in Figure 4.18 has three peaks. The major reduction occurred at the temperature of 520 °C and the other two peaks occurred as small shoulders. When compared to the TPR profiles of the monometallic samples, the first peak that occurred at 340 °C is easily assigned to the reduction of Sn oxide. The reduction peaks at 440 °C and 520 °C correspond to the co-reduction of the Sn and Re oxides according to Carvalho et. al (2004, pg. 8). However, there are no higher reduction temperature occurred that could signified the reduction of Re oxide as has been obtained by Carvalho (2004, pg. 8) where in the same research he had noted that the TPR peaks of the Re–Sn system are located at a higher temperature than those of Sn and Re alone, indicating a strong interaction between Re and Sn oxides and with alumina. Others than that, he also observed that the area of hydrogen consumption of Re–Sn is smaller than the sum of the areas of Re and Sn, and this is due to a smaller degree of reduction of the interacting oxides.

5.5 Supported Tri-metallic Catalysts

TPR of Pt-Re-Sn/Al_2O_3

The TPR plot of the tri-metallic Pt-Re-Sn/Al_2O_3 catalysts in Figure 4.19 gave five reduction peaks with two distinct reduction peaks occurred at the temperature of 260 °C and 410 °C. Carvalho et. al (2004, pg.8) had found similar result and he concluded that the very intense peak at about 260 °C is due to reduction of Pt oxide and a small fraction of Sn and Re oxides. The intermediate region at about 270–450 °C can be assigned to the Pt-catalyzed reduction of Re and Sn oxides and finally a third peak at 450–800 °C is due to the reduction of segregated Re oxide and small amounts of Sn oxide. Strong bonded might also occurred between Re and Sn oxides or with the support that caused them not to be reduced during the experiment.

CHAPTER 6

CONCLUSION AND RECOMMENDATION

6.1 Conclusion

This research was intended to cover the bimetallic catalysts systems, the method of preparing and characterizing them and the reactions. However, due to time constraints, the scope of the research has been narrowed down to characterizing the catalysts by using the temperature programmed reduction (TPR). Nevertheless, literature reviews has been done throughout the research in order to obtain information regarding the bimetallic catalysts. Though the main objective of the project is to study the bimetallic catalysts systems (Pt-Re/Al_2O_3, Pt-Sn/Al_2O_3 and Re-Sn/Al_2O_3) but the monometallic catalysts (Pt/Al_2O_3, Re/Al_2O_3 and Sn/Al_2O_3), the tri-metallic catalysts (Pt-Re-Sn/Al_2O_3) and the support (γ-Al_2O_3) had also been included for characterizing.

In the temperature programmed reduction (TPR) analysis, the reduction temperatures of each catalysts has been determined. The reduction temperature is the temperature at which the hydrogen is energetically enough to be converted into water vapor at that temperature. The reduction temperatures for all the catalysts are summarized in table 4.5 in Chapter 4. The result shows that the bimetallic catalysts have lower reduction temperatures than the monometallic catalysts reduction temperatures of the tri-metallic catalysts are even lower compared to the monometallic catalysts and the bimetallic catalysts.

The temperature at which reduction occurs and the number of reduction peaks depend on the oxidation state of the metals, the interaction of the oxides among them and with the support and on the possible catalytic action of Pt or other elements present or generated during reduction. The significance of low reduction temperature is it indicate a better activation capability therefore the bimetallic catalysts and the tri-metallic catalysts are considered good and effective for the industry since the reduction temperatures are low compared to the monometallic catalysts.

6.2 Suggested Future Work for Expansion and Continuation

Since the introduction of rhenium as a promoter to catalytic activity of Platinum in 1968, more other bimetallic catalysts system has been developed such as Pt-Sn, Pt-Ge and Pt-Ir. The addition of the second metal to the Platinum has been observed to improve the catalytic activity of Platinum. The bimetallic catalysts are more selective and stable than Pt monometallic catalyst and allow the process to be run at a lower hydrogen pressure. Seeing the importance of these catalysts to the reforming industries, it is important to study the properties of the catalysts and its relationship to the catalytic performance. The TPR technique has been chosen to study the reactivity of the catalysts surface in this project.

Few recommendations for further continuation of this study:

- Do more literature reviews on the characterization techniques such as for comparing with the work done on bimetallic catalysts by other researchers.
- Do pretreatment on all the catalysts before doing the TPR analysis.
- The TPDRO should be connected to a mass balance in order to check for the release of unrelated organic material.
- Re-oxidized the reduced catalysts before being reduced again. By doing this, the interaction between the metals can be studied for the condition in which the catalysts had been re-oxidized.
- Do other characterization techniques such as the XRD to compare the result obtain by other technique and can try to use other TPR equipment in order to check for the reproducibility of the results.

REFERENCES

1. Farrauto, R.J and Bartholomew, C.H. 1997, *Fundamentals of Industrial Catalytic Processes*, London, Blackie Academic & Professional.

2. Jones and McNicol, 1986, *Temperature-Programmed Reduction for Solids Materials Characterization*, United States of America, Marcel Dekker, Inc.

3. Rase, 2000, *Handbook of Commercial Catalysts (Heterogeneous Catalysts)*, United States of America, CRC Press LLC

4. Page, 1987. *Applied Heterogeneous Catalysis*, France, Editions Technip.

5. Spindel, W.1992. *Catalysis Looks to the Future*, National Academy Press.

6. Hagen, Jens. 1999. *Industrial Catalysis*, New York, WILEY-VCH.

7. Satterfield, C.N, 1991. *Heterogeneous Catalysts in Industrial Practice (2)*, New York, McGraw Hill Inc.

8. Thermo Finnigan Italia S.P.A, 1998. TPD/R/O 1110 Instruction Manual, Milan.

9. Szynkowska, Loshiewska and Paryjezak. 2003. *Temperature Programmed Techniques in Catalysis*, *Polish J. Chem*, 77, 657 – 673

10. Carvalho, Pieck, Rangel, Figoli, Reyes and Perera. 2004. *Applied Catalysis A. 269,91 – 103*

11. Larsson. 1997. *Thesis: Coke on supported Palladium and Platinum Catalysts, Goteborg, Sweden.*

12. Silvia, Santos, Mandes, Jordao and Faraga . 2003, *Applied Catalysis A*, 241, 155 – 165

13. Lieske and Volter, 1984, *J.Catalysis*, 90, 96 – 105

14. Pieck, Gonzalez and Parera. 2001. *Applied Catalysis A*, 205, 305 - 312

15. Llorca, Homs, Leon, Sales, Fierro and Piscina. 1999, *Applied Catalysis A*, 189, 77 – 86

16. Neri, Milane, Galvagno, Pijpes and Schwank. 2002, *Applied Catalysis A*, 227 105 -115

17. Carnevillier, Epron and Marecot. 2004. *Applied Catalysis A*, 275, 25 – 33

18. http://www.editionstechnip.com.sources

19. http://www.mpopc.org.my/ebtenfu.html

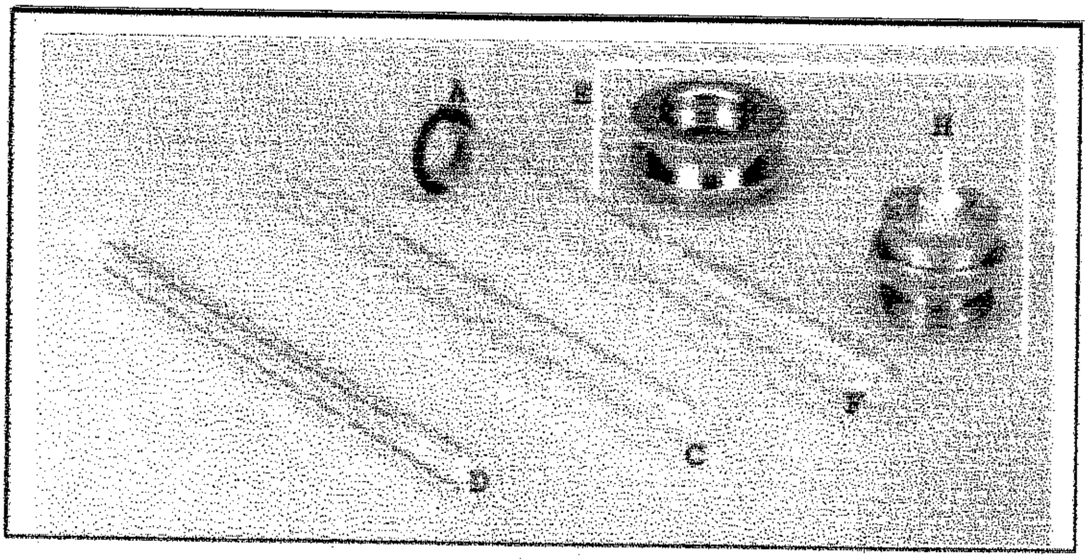
20. http://www.tintechnology.biz/tintechnology/tintechnology

21. http://www.mii.org/Minerals/photorhenium.html

22. http://www3.interscience.wiley.com/cgi-bin/summary/104552131/SUMMARY

APPENDICES

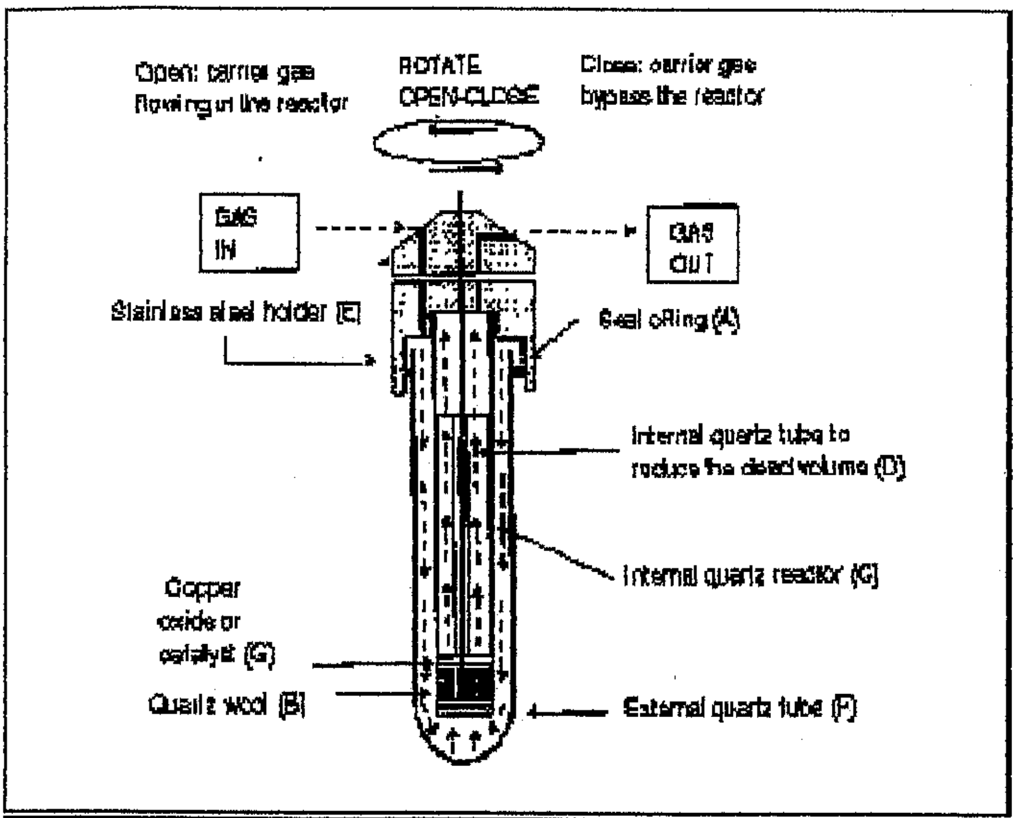
APPENDIX 1: REACTOR USED FOR TPR ANALYSIS (THERMO FINNIGAN 1100)



A. O-ring	E. Stainless steel holder and nut
C Quartz internal bulb	F. Quartz external bulb
D Quartz tube for volume reduction	H. Stainless steel fitting

The reactor, shown in figure above consists of the following parts:

- Stainless steel holder **E** and relevant nut for fixing the reactor. An internal mechanical arrangement allows to insulate the sample from the atmosphere by rotating the fitting top.
- Two flexible tubes equipped with quick-fit connections allow to connect the system with the inlet (IN) and outlet (OUT) gas lines. \
- The stainless steel fitting **H** on the reactor head **E** is available in two versions.



A. O-ring	**B. Quartz wool**
C. Quartz internal bulb	**D. Quartz tube for volume reduction**
E. Stainless steel holder and nut	**F. Quartz external bulb**
G. Copper oxide or catalyst	**H. Stainless steel fitting**
GAS IN. Gas inlet connection	**GAS OUT. Gas outlet connection**

1. Remove the stainless steel nut from the reactor holder E.
2. Mount the triangular O-ring **A** onto the external bulb **F** (the flat section turned down).
3. Introduce a wad of quartz wool **B** into the internal bulb **C** and push it down to the bottom to close the hole.
4. Insert the volume reduction tube **D** into the bulb **C** resting it on the quartz wool.
5. Introduce the bulb **C** into the holder **E** pressing gently to make it enter the appropriate hole, in a way that the internal seal (not removable) is sealingly in place.
6. Insert the external bulb **F** onto the internal bulb **C** to have the triangular O-ring **A** match the stainless steel holder.
7. Insert the stainless steel nut into the external bulb **F** and screw it on the holder.

Samples For Thermo Finnigan TPDRO 1100

Date	
Producer	
Sample Name	
Weight of Sample Holder and Sample	
Weight of EMPTY Sample Holder	
Type of Analysis	

Sample Information

Metal Supported ○ Mixed/Pure Oxides ○ Other ○ ______________

Metal type (1) __________ Metal (1) % __________

Metal type (2) __________ Metal (2) % __________

Metal type (3) __________ Metal (3) % __________

Support Type: ______________

Sample Pretreatment

1. Gas ______________ Flow (cc/min) __________ Start T (°C) ______
   Rate (°C/min) ______ Final T (°C) ______ Holding (min) __________
2. Gas ______________ Flow (cc/min) __________ Start T (°C) ______
   Rate (°C/min) ______ Final T (°C) ______ Holding (min) __________
3. Gas ______________ Flow (cc/min) __________ Start T (°C) ______
   Holding (min) __________
4. Gas ______________ Flow (cc/min) __________ Start T (°C) ______
   Holding (min) __________

ANALYSIS

TPD/R/O Gas ______________________ Flow (cc/min) __________
Start T (°C) __________ Rate (°C/min) ______ Final T (°C) ______ Holding (min) ______

Pulse At T (°C) __________ Gas ______________ Flow (cc/min) ______
# of Pulses ______

Preparation, Characterizations and Reaction
of
Bimetallic Catalyst for Reforming

By:

Marlinne Goven

Dissertation submitted in partial fulfillment of
The requirements for
Bachelor of Engineering (Hons)
(Chemical Engineering)

November 2004

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Certification of FYP Final Draft Submission

Herewith I, (Marlinne Goven,1811) certify that I am responsible for the work submitted in this project, and I have done all the modifications according to my supervisor's advice.

Thank you.

	Submit by Student	Verify by Supervisor
Signature		
Name	Marlinne Goven	Dr,Chong Fai Kait
Student ID	1811	
Date	2 November 2004	2 November 2004

CERTIFICATION OF APPROVAL

Preparation, Characterization and Reaction of Bimetallic Catalysts for Reforming

By

Marlinne Goven

A project Dissertation submitted to the
Chemical Engineering Program
Universiti Teknologi PETRONAS
In partial fulfillment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

(Dr. Chong Fai Kait)
Main Supervisor

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
November 2004

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and the acknowledgements, and that original work contain herein have not been undertaken or done by unspecified sources or persons.

(MARLINNE GOVEN)

ABSTRACT

This study has been done to characterize the bimetallic catalysts which consist of the Pt-Re/Al_2O_3, Pt-Sn/Al_2O_3 and Re-Sn/Al_2O_3 catalysts by using temperature programmed reduction (TPR). For comparison, the support (γ-Al_2O_3), the monometallic catalysts (Pt/Al_2O_3, Re/Al_2O_3 and Sn/Al_2O_3) and the tri-metallic catalyst (Pt-Re-Sn/Al_2O_3) were also being characterized by using the same technique.

Platinum-on-alumina catalyst had been introduced to the industry in 1949 since it have dual function of providing both the acidic sites and metallic sites that are important for reforming reaction. Beginning in 1970s, it was introduced as having one or more additional metallic components including rhenium and tin. These bimetallic catalysts exhibit greatly improved stability (cycle length) and selectivity.

The TPR analysis is based on the reducibility of species in the solids which enables one to obtain information not only of a purely analytical nature but also and more importantly, about the condition of species present in and on solids. This technique allows the determination of the temperature at which the reduction itself takes place as the function of the flows conditions, the percentage of a reactive gas, the quantity of samples and the speed of the temperature increase.

Based on the TPR analysis, bimetallic catalysts and the tri-metallic catalysts are observed to have lower reduction temperatures than the monometallic catalysts and are concluded to have better catalytic activity. The temperature at which reduction occurs and the number of reduction peaks depend on the oxidation state of the metals, the interaction of the oxides among them and with the support and on the possible catalytic action of Pt or other elements present or generated during reduction. The significance of low reduction temperature is it indicates a better activation capability therefore considered good and effective for the industry.