# TEMPERATURE PROGRAMMED CHARACTERIZATION OF SPENT SYNGAS CATALYSTS

# ($NiO/MgOAl_2O_3$)

by:

Rozalina Shiela binti Ramlan (2896)

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

JULY 2005

Universiti Teknologi PETRONAS
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Perak Darul Ridzuan

# 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 aspect as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified source or person.

ROZALINA SHIELA BINTI RAMLAN

# CERTIFICATION OF APPROVAL

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# ABSTRACT

This research project is conducted to determine the properties of fresh and spent NiO/ $MgOAl_2O_3$, which is syn gas catalyst by using temperature programmed method. The main deactivation process on syngas catalyst is coke deposition, which can be observed on the spent catalyst. The scope of study includes a thorough literature research on nickel based catalyst for steam reforming from various sources of journals through internet and books.

The temperature programmed method including Temperature Programmed Reduction (TPR) and Temperature Programmed Oxidation (TPO). The author has utilized several methods such as TPR, TPO, SEM/EDX and FTIR, which led to significant findings in this area of study.

For TPR result, there are three reduction peaks for fresh catalyst (230°C, 445°C and 605 °C) and four reduction peaks for spent catalyst (200°C, 460°C, 530°C and 800°C). From FTIR analysis, the functional groups on fresh and spent catalyst have been identified. The –OH functional group is identified in fresh and spent catalyst but nitrate group only found in fresh catalyst. EDX result show loss in nickel content for spent catalyst compare to fresh catalyst. This loss is due to sintering of catalyst. Two sets of regeneration procedure has been design; regeneration at 400°C and 600°C, both in oxygen atmosphere.

# ACKNOWLEDGEMENT

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Foremost gratitude goes to Dr. Chong Fai Kait for all the guidance through the period of this study as supervisor without loosing her patience. This study and project works may not be able to be completed without her advice and supervisions. It was an irreplaceable eye opener being under her supervision throughout the study and project.

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Special thanks to Chemical Department Technician and Mechanical Department technicians, Encik Asnizam Helmy especially, who have willingly provided the author with help and sharing their expertise.

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# INTRODUCTION

## 1.1 Background of Study

Today, hydrogen has emerged as a clean energy source offering an alternative to the fossil fuels. This gas can be directly burnt in an internal combustion engine or electrochemically converted to electricity in a fuel – cell system. Neither of these processes produces carbon dioxide, soot or carbon monoxide.

In particular, the reforming of methane with steam is the leading method of hydrogen production in the world, owing to the great volume of natural gas, consisting mainly of methane, produced annually.

In industry, this is a catalytic process, in which nickel – based catalyst is utilised, supported on refactory materials such as $Al_2O_3$ and $MgAlO_4$, to which some stability promoter, is added such as $K_2O$ and $SiO_2$.

However, some potential problems may arise owing to the need to operate at high temperature. The thermal stability of the catalyst is certainly one, the steam tending to promote the sintering of the support and the catalyst, but for a nickel catalyst, the main problem is coke formation, which follows the simplified mechanism below:

$CH_4 \rightarrow C + 2H_2$ ---------------------------------------------------------------- (1)

$2CO \rightarrow C + CO_2$ -------------------------------------------------------------- (2)

$CO + H_2 \rightarrow C + H_2O$ ---------------------------------------------------------- (3)

$C_nH_{2n+2} \rightarrow nC + (n+1)H_2$ ---------------------------------------------------- (4)

In fact, the need to minimize the deposition of coke is one of the biggest limiting factors for the industrial application of steam reforming. Considering reaction (3), the most obvious way to minimize coking is to increase the steam: carbon ratio, in order to favor the reverse reaction and this method is used in industrial processes. However, the provision of steam at high temperature is expensive, which tends to cancel out any significant economic advantage achieved by the reduced carbon deposition under stoichiometric conditions.

Apparently, this deposition during steam reforming of methane occurs predominantly by methane decomposition reaction (1). The catalytic production of hydrogen by methane decomposition was used in the past, consisting in the passage of methane alone over a metallic catalyst to form hydrogen and coke, the coke being deposited on the catalyst. After a predetermined time, the catalyst needs to be regenerated by passing air over it at high temperatures to burn off the deposited carbon through reactions (7) and (8):

$C + \frac{1}{2} O_2 \rightarrow CO$ ---------------------------------------------------------------------------- (7)

$CO + \frac{1}{2} O_2 \rightarrow CO_2$ -------------------------------------------------------------------------- (8)

Although the supported noble metals such as rhenium, platinum, iridium, pyrochlore and perovskite oxide –possesses excellent resistance to coke deposition, their uses are limited by their extremely high cost (Claridge, Tsang, York and Ashcroff Battle, 1993). Therefore, it is desirable to develop nickel – based catalyst with good resistance to coke.

Commercially, this $CH_4$ reforming utilizes nickel catalyst supported on alumina, MgO or $MgAl_2O_4$. But the disadvantage of this process is excessive coke formation which is believed to be caused by the sintering of metallic nickel particles, leading to catalyst deactivation.

Catalyst deactivates in four ways; sintering, poisoning, coking and pore collapse. Sintering in the major problem in the life of catalyst since it involves loss of active surface area. Most of the time, sintering occurs due to the exposure to high temperature. Therefore, it is call thermal deactivation.

Poisoning of the catalyst occurs by the adsorption of impurities from the feed on the specific catalyst sites. The most common causes for poisoning is the chemisorptions of gaseous species on the active sites of the catalyst, such as nitrogen and sulfur compounds. Pore collapse is one of the catalyst deactivation cause by sintering of the support and leading to loss of surface area and porosity.

The coke deposition during steam reforming is formed by methane itself and carbon monoxide, which can be determined by the simplified mechanism below. The catalyst need to be regenerated by passing air over it at high temperature to burn off the deposited carbon, either by oxidation or partial oxidation.

$$CH_4 \rightarrow C + 2H_2$$

$$2CO \rightarrow C + CO_2$$

Coke deposition can be removed by regenerating the spent catalyst. The oxidative regeneration should be well controlled to minimize the local overheating from oxidation of nickel and carbon. Catalyst can suffer sintering or chemical transformation in the active phase when they are exposed to oxidative stream. In the case of Ni catalyst where the alkali or metallic promoters are commonly added to the catalyst in order to enhance regeneration. Andrew has suggested that alkali moves across the nickel surface to accelerate the removal rate of carbon residues (Andrew, 1996)

Steam reforming process could extract the hydrogen not only from hydrocarbons but also from water and the reaction rate is very fast. However, this process is accompanied by unfavorable and undesired formation of different carbonaceous deposits or coke, which deactivates the catalyst. Therefore, this research project is going to characterize

$NiO/MgOAl_2O_4$ and design an appropriate regeneration procedure with optimum condition to remove coke deposited effectively.

## 1.2 Problem Statement

### 1.2.1 Problem Identification

The catalyst surface become deactivated after a certain period of operation, which is caused by several factors such as thermal sintering, pore collapse, sulfur and nitrogen poisoning. The main deactivation process on syngas catalyst is coke deposition, which can be observed on the spent catalyst.

During operation of the reformer system, carbon formation external and / or internal catalyst particles are possible. Carbon deposits outside the particles will increase the pressure drop over the catalyst bed and deposits inside will reduce the activity and the mechanical strength of the catalyst. To overcome this problems, spent catalyst regeneration procedure need to be designed.

### 1.2.2 Significance of the project

This project involves characterization of the spent and fresh catalysts for steam reforming using temperature programmed technique and some instrumental methods. It was conducted to study the catalyst's characteristic and catalytic performance. The information gathered on the spent and fresh catalyst is used to design an appropriate regeneration procedure for spent syngas catalyst.

## 1.3 Objectives and Scope of Study.

There are two objectives that need to achieve in this projects:

a) To determine the properties of spent and fresh syngas catalysts by using Temperature Programmed Method (TPDRO 1100).
b) To design spent syngas catalysts regeneration procedure.

The scope includes a thorough literature research on nickel based catalyst for steam reforming from various sources of journals through internet and books. The experiments were conducted at Universiti Teknologi PETRONAS.

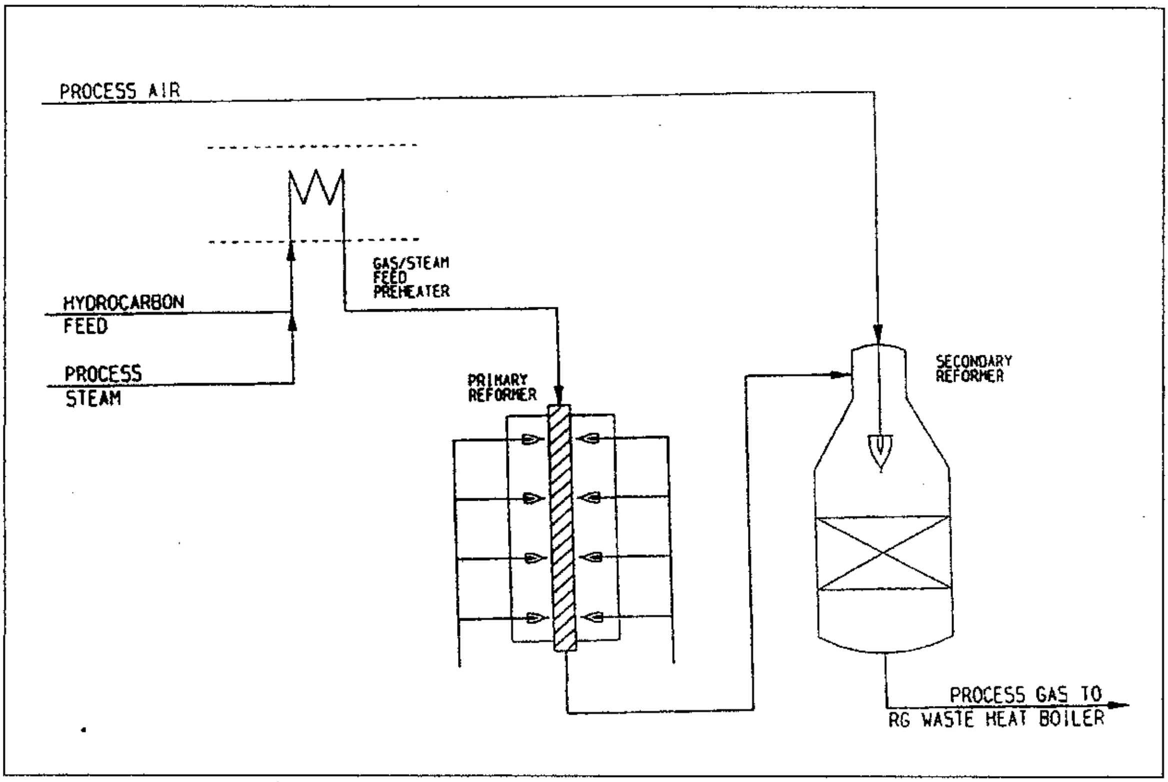


Figure 2.1: Reformer system Process Flow Diagram

### 2.1.1 Primary Reformer

The first step of the steam reforming process takes place in the primary reformer. In it, the hydrocarbon and steam mixture, which is preheated to 520 – 535°C, is passed down ward through vertical tubes containing catalyst. The primary reformer is a fired heater in which the sensible heat and the heat of reaction are transferred by radiation from a number of wall burners to the catalyst tubes.

In order to ensure complete combustion of the fuel gas the burner are operated at an excess air ratio of about 5% which corresponds to 0.9% of oxygen in the flue gas.

The hydrocarbons in the feed to the primary reformer are converted into hydrogen and carbon oxide. The outlet gas, leaving the primary reformer, contains approximately 11 –

14 mole% of methane. The exit temperature of the primary reformer is about 800°C, which is the inlet temperature to the second step of the reforming.

### 2.1.2 Secondary Reformer

In the secondary reformer, the process gas is mixed with air. The partial combustion takes place in the top part of secondary reformer and causes a considerable increase in temperature. From the "combustion chamber", the gas passes down through a catalyst bed in which the final part of the reforming takes place with simultaneous cooling of the gas. The temperature of the process gas leaving the secondary reformer is about 960°C and the methane concentration is approximately 0.60 mole%.

The exit gas from the secondary reformer contains about 13mol% CO and about 8mol% $CO_2$. Consequently, there is a theoretical risk of carbon formation according to Bourdouard reaction:
$2CO + CO_2 \rightarrow CO_2 + C$ (as soot)
The lower limit for the reaction is 650°C as the reaction rate becomes too slow at lower temperatures.

The catalyst bed rests on a layer of alumina lumps and at the top of the catalyst bed a layer of alumina balls and alumina tiles protects the catalyst from agitation and direct flame contact. The combustion of the process gas with air gives a gas temperature of 1100 – 1200°C in the upper part. As the reforming reaction of methane absorbs heat, the outlet temperature of the secondary reformer is approximately 960°C.

In the temperature range of 1400 - 1500°C, the catalyst starts sintering. The activated catalyst may never be exposed to air at temperatures above 1000°C as this will cause spontaneous heating which may lead to overheating and destruction of the catalyst due to the "snow – balling" effect.

## 2.2 Ni/MgOAl$_2$O$_3$ Catalysts

Dry reforming of methane for the production of syngas has attracted much attention from both industrial and environmental aspects. As mention before, steam reforming is divided into 2 categories, which are primary reforming and secondary reforming.

Although the chemical reaction in the secondary reformer are more or less the same as those of the primary reformer, the combustion of air in the secondary reformer will give high gas temperature at the top of the catalyst bed, call for a catalyst, where high thermal stability and mechanical integrity is mandatory.

Guo et al., 2004 has reported that, another obstacles encounter in the application of this process is rapid deactivation of the catalyst, which is mainly due to coke accumulation and sintering of both the support and the active metal particles.

A variety of catalysts have been developed for this reaction. Among them, the catalysts based on noble metals are reported to be less sensitive to coking than nickel – based catalysts. Considering the high cost and limited available of noble metals, however, it is more profitable to develop a Ni – based catalyst, which is resistant to coke accumulation and exhibits long term stability (Guo et al., 2004).

Suitable supports have to be resistant to high temperature applied and they have to maintain the metal dispersion of the catalyst during operation. Bhattacharyya et al., 1994 have recently proposed to use the nickel spinel catalyst in order to reduce coke formation in CH$_4$/CO$_2$ reforming.

Magnesium aluminate spinel (MgAl$_2$O$_4$) offers a desirable combination of properties for use in ceramics, due to its high melting temperature (2135°C), good chemical stability and mechanical strength. Due to its low acidity and sintering – resistance, such spinel has been widely studied as catalyst support for catalytic steam reforming of methane (Guo et al., 2004).

## 2.3 Catalyst Characterization

### 2.3.1 Temperature Programmed Techniques.

Temperature-programmed techniques have been the most widely used methods in characterizing chosen properties of catalysts. According to International Conference of Thermal Analysis (ICTA) in 1979, thermal analysis is a group of techniques, in which physical properties of substance or products of reaction taking place are measured as a function of temperature, while the substance studied is undergoing a controlled program of temperature change. Temperature-programmed techniques are particularly useful in the study of interactions between reactants and catalyst's surface including catalytic reaction, as well as adsorption of gases on metals and metal oxides (Szynkowska et al., 2003)

Temperature-programmed techniques are used in a variety of heterogeneous studies such as:

- Determination of selective surface of metals and their dispersion.
- Determination of interaction between components of catalysts.
- Determination of optimal conditions of catalysts' regeneration.
- Study of catalysts' deactivation.
- Study of carbon deposit

According to Szynkowska et al.,2003, in temperature-programmed techniques the shape and position of peaks depend on many factors, which should be taken into account in the experiment, in order to decrease all diffussion effects in the first place, and also subsurface diffusion, adsorption and desorption.

Figure 2.2 shows the basic scheme of apparatus, which is used in temperature-programmed techniques. Major elements of apparatus are: a reactor, temperature-programmed furnace, purifying system and a dosage system for carrier gas and reactant gases, a system for chemical analysis.

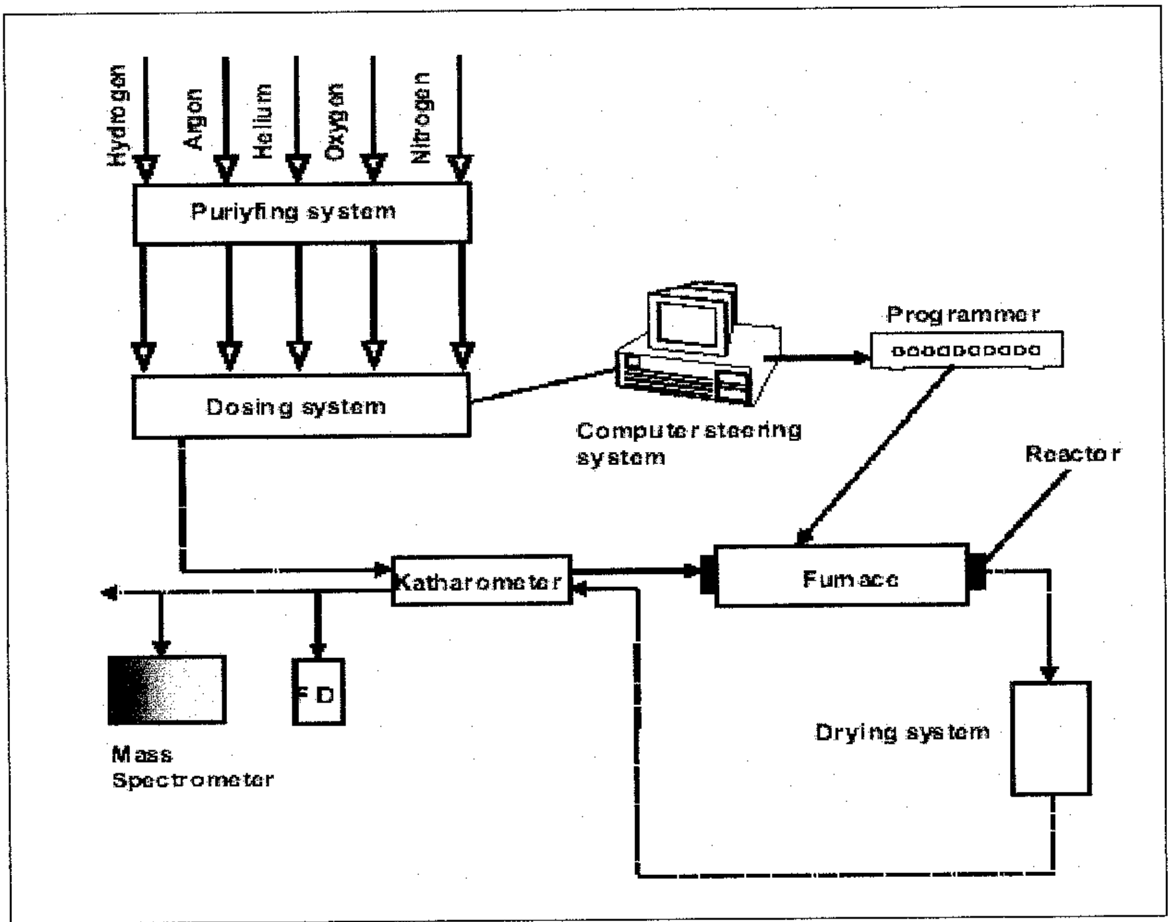


Figure 2.2: The scheme of the system used in temperature-programmed techniques (Source: Szynkowska et al.,2003)

The temperature programmed techniques used in this area of study are Temperature Programmed Reduction (TPR) and Temperature Programmed Oxidation (TPO).

i) Temperature Programmed Reduction (TPR) Techniques.

TPR analysis is used to determine the temperature at which reduction take place for the species. It also provides characterization of the catalyst which is able to analyze the number and quantity of the reducible species present in the sample (Thermo Finningan, 1998).

The basic set up for the TPR consists of a reactor and thermal conductivity detector (TCD). TCD is used to measure the amount of hydrogen being consumed and the temperature at which the reduction take place.

The example of $H_2$ – TPR results of the catalysts are given in Figure 2.3, which displays the normalized TPR profiles of the $Ni/Al_2O_3$ and $Ni/MgO\text{-}Al_2O_3$ catalysts calcined at 550°C, as well as that of a pure NiO sample, which was calcined at 800°C. Two reduction peaks were observed for $Ni/Al_2O_3$ and $Ni/MgO\text{-}Al_2O_3$ catalysts around 500 – 600°C and 600 – 900°C (Guo et al., 2004).

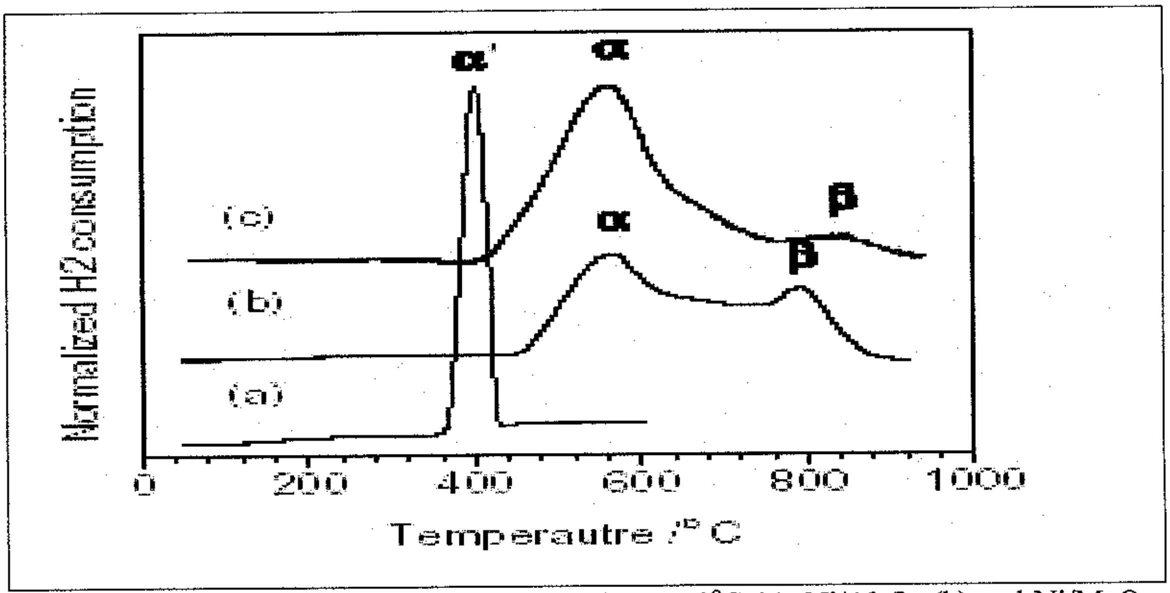


Figure 2.3: TPR profile of NiO calcined in air at 800°C (a), $Ni/Al_2O_3$ (b) and $Ni/MgO\text{-}Al_2O_3$ (c) calcined in air at 550°C.(Source: Guo et al., 2004).

ii) Temperature Programmed Oxidation (TPO) Techniques.

TPO analysis is used to determine the temperature at which oxidation take place in the catalyst. TPO can be used for:

- Characterization of redox properties of metal and metal oxides.
- Characterization of coke species in deactivated catalysts.
- Total coke content in deactivated catalysts.
- Mechanism and kinetics of oxidation reactions.

The quantity and quality of carbon deposited on Ni/La - $AlO_3$ and Ni/α - $Al_2O_3$ after reaction for 24 h were thus evaluated by means of TPO measurements, is one of the example the application of TPO. The results are shown in Figure 2.4

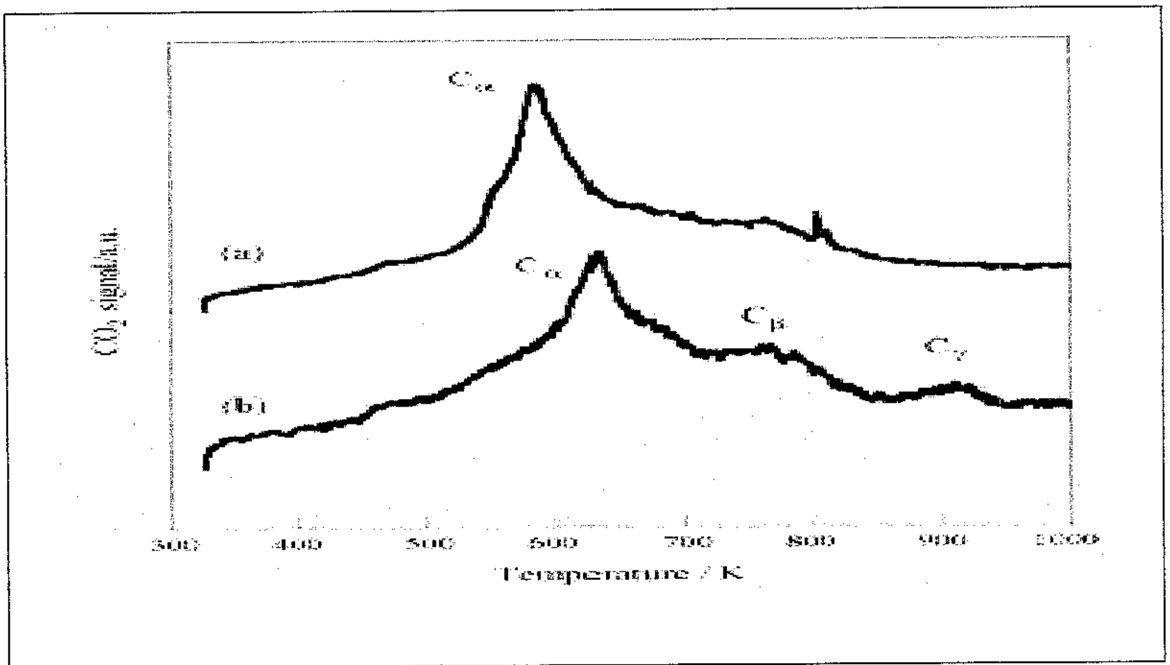


Figure 2.4: Temperature programmed oxidation for (a) Ni/$LaAlO_3$ and (b) Ni/α - $Al_2O_3$ after reaction for 24 h. (Source: Urusaki et al., 2005)

In the case of Ni/α -$Al_2O_3$ which was deactivated gradually during the activity test, three peaks were observed: around 623, 773 and 923 K. In contrast, Ni/$LaAlO_3$ gave only one peak at around 623 K (Urusaki et al., 2005)

The carbon deposited was obtained by using mass spectrometry that measures the intensity of $CO_2$, the oxidation product of the deposited carbon, as a function of linearly increased sample temperature.

### 2.3.2 Thermogravimetric Analysis (TGA)

Dias et al., 2004, stated that TGA analysis is used to determine the amount of carbon formed, which shows the total loss of mass relative to the mass of catalyst, attributed to the removal of accumulated carbon.

Urusaki et al., 2005 in their report has used TGA in order to understand the oxidation – reduction properties of Ni/perovskites. Figure 2.5 shows the weight loss of used nickel catalyst and fresh catalyst as a function of temperature.

Every Ni/$LaAlO_3$ showed a decrease in weight starting around 600 K. The observed weight loss can be considered to correspond to the reduction of nickel oxide. However the amount of weight loss was larger than the 26.5 mg g-cat_1 loss caused by the reduction of nickel oxide. The excess weight loss is caused by the reduction of $LaAlO_3$.

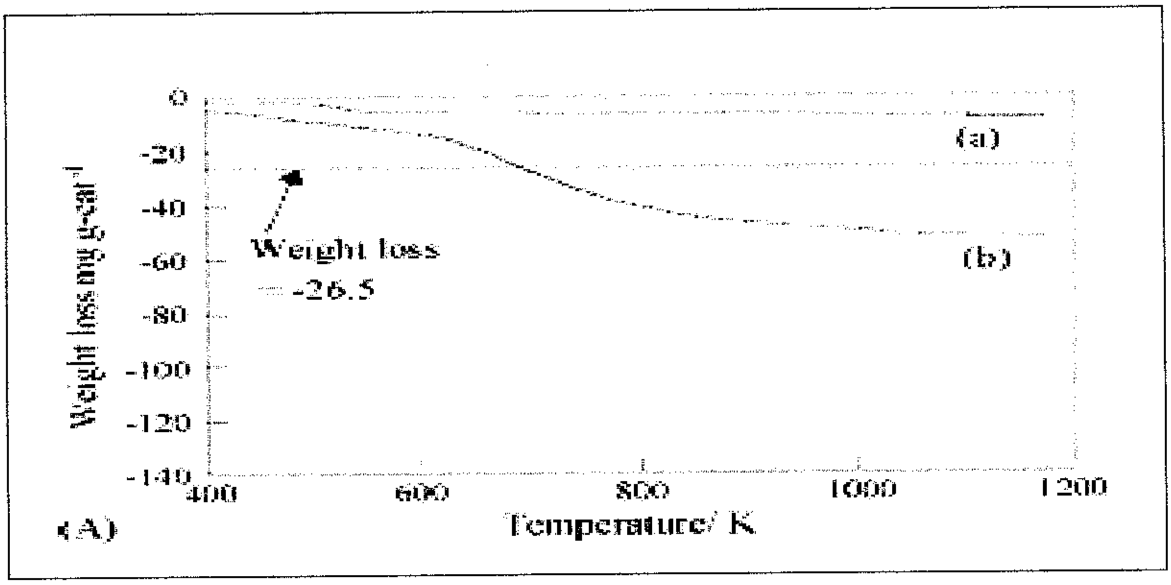


Figure 2.5: Thermogravimetric analysis of Ni/$LaAlO_3$ (a) used catalyst and (b) fresh catalyst. (Source: Urusaki et al., 2005)

### 2.3.3 Scanning Electronic Microscopy (SEM)

SEM is used to observe the morphology of the carbon deposited (Dias et al., 2004). It also enables the imaging of the topography of a solid surface by application of backscattered or secondary electrons, with resolution, at present of better than 5nm (R.J. Farrauto and C.H. Bartholomew, 1997).

The application of SEM can be shown by taking image of Ni/$Al_2O_3$ after 8h of steam reforming as an example.

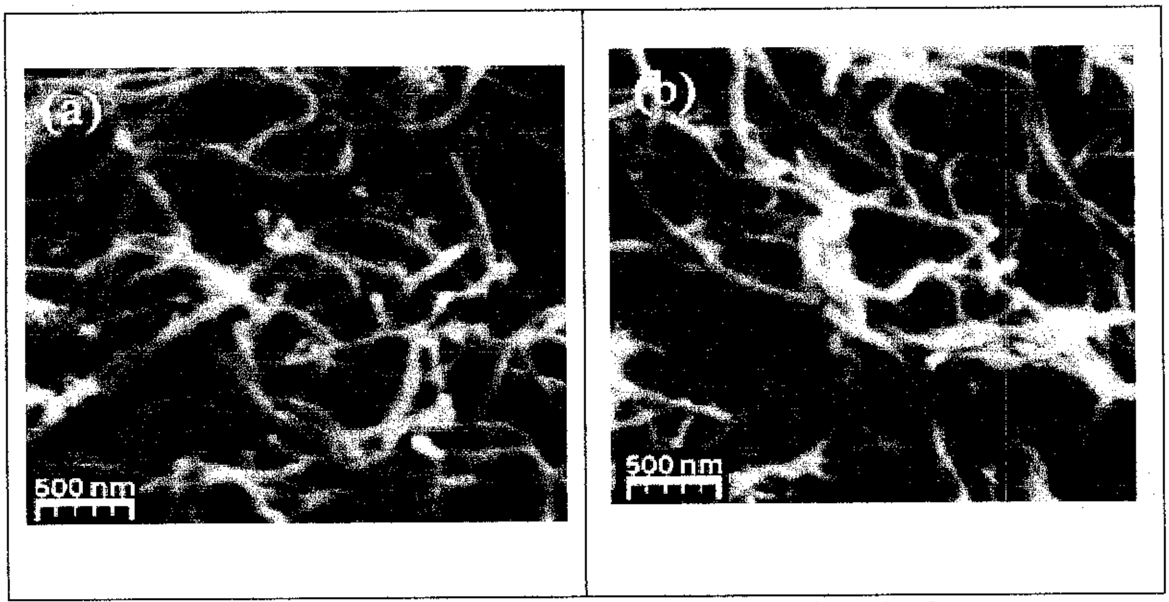


Figure 2.6: Scanning electron microscope image of $Ni/Al_2O_3$ after 8 h of steam reforming, with magnification of 30,000×. Ratio $O_2/CH_4$: (a) 0; (b) 0.04 (Source: Dias et al., 2004)

Figure 2.6(a) shows micrographs of a sample submitted to steam reforming without the addition of air, which verify the hypothesis of carbon filament formation, as the deposit consists mainly of this phase. The average diameter of carbon filaments shown in Figure 2.6(a) is around 150 nm (Dias et al., 2004).

### 2.3.4 CHNS Technique

The CHNS instrument can determine the carbon, hydrogen, nitrogen and sulfur content for homogenous material. High temperature combustion is used as means of removing the elements from the material. In the combustion process, a nominal 2 mg sample is encapsulated in a tin or silver capsule.

The sample is then placed in the sample loading chamber and held there until a dose of oxygen has been released. The sample is then dropped into the furnace at the same time when the oxygen has been released. The sample is combusted by the heated oxygen – rich environment.

### 2.3.5 Fourier Transform Infrared Spectroscopy (FTIR) Technique

Fourier Transform Infrared (FTIR) spectroscopy uses a narrow portion of the electromagnetic spectrum. The infrared spectrum is divided into three regions; which are near infrared (NIR), middle infrared (MIR) and far infrared (FIR). NIR routinely used for process quantitative analysis, MIR involved with molecular vibration and FIR concerned with rotational spectra and crystal lattice vibrations.

IR spectroscopy is also known as vibrational spectroscopy since the spectra arise from the transitions between the discrete vibrational energy levels of a molecule. FTIR was used to identify the functional group of coke and compare the spectra functional group between fresh and spent samples.

## 2.4 Regeneration Method for Deactivated Catalysts

Steam reforming of methane, which has been used for large – scale hydrogen production in industrial processes such as petroleum refinery and ammonia synthesis, has become increasingly important recently because of its potential applications in fuel cell. (Villacampa et al., 2003).

As the steam reforming reaction is strongly endothermic, the process requires reaction temperature higher than 1000K and an excess amount of steam to prevent coking on the catalyst (Urasaki et al., 2005). However, high reaction temperatures and the use of excess steam caused an increase in the amount of energy consumed and consequently in the hydrogen production cost.

Guo et al.,2004, reported that Ni – based catalyst is profitable to be developed for steam reforming since it is resistant to coke accumulation and exhibit long – term stability. Thus, some potential problems can arise from the need to operate at high temperature. The thermally stability of the catalyst is certainly one, the steam tending to promote the sintering of the support and catalyst, but for a nickel catalyst, the main problem is coke formation (Dias et al., 2004).

In fact, the need to minimize the deposition of coke is one of the biggest limiting factors for the industrial application in steam reforming. Considering reaction, the most obvious way to minimize coking is to increase the steam: carbon ratio, in order to favor the reverse reaction and this method is used in industrial processes (Dias et al., 2004).

In the literature by J. A. C. Dias, 2004 and J. M. Assaf, 2004, it is known that the formation of carbon involves a carbide cycle and consists of two to three steps: the first step is the formation of a monolayer of carbon atoms through intermediate carbide – like compound. This species is highly reactive and easily removed.

The second step includes the formation of a graphite phase by polymerization of the carbon atoms, when they are in excess. These graphite deposits can accumulate over the metal surface, deactivating it. In metal particles bigger than 5nm, a third step can occur, in which the high concentration of carbon at the top surface cause a concentration gradient between this surface and the bottom of the particle, which leads to carbon diffusion across the nickel crystal.

Due to sintering and coke formation problems, the catalyst needs to be regenerated in order to recover the activity, reactivity and stability. Some of the regeneration procedures for Ni – based catalyst from various sources are simplified in Table 2.1.

Table 2.1: Regeneration Procedure for Syn gas Catalyst

| Catalyst | Regeneration Procedure | Remarks |
|---|---|---|
| $Ni/Al_2O_3$<br>(J. A. C. Dias and J. M. Assaf, 2004) | Steam reforming:<br>Regeneration catalyst by passing air over it at high temperature to burn of the deposited carbon. | The addition of air to the steam reforming feed results in a decrease in the amount of carbon formed on the catalysts. |
| $Ni/Al_2O_3$<br>(J. I. Villacampa et al., 2003) | Methane reforming:<br>Regeneration with higher reduction temperature about 900°C under a $H_2/N_2$ mixture. | - Increase the degree of sintering of the Ni crystallites resulting in the formation of a smaller number of filaments.<br>- Drastic sintering of the Ni crystallites resulting in a sharp reduction in the number of carbon filaments formed.<br>- After the regeneration step, the metal – support interaction is very low. |
| Ni – MgO<br>(A. Shamsi, 2004) | Methane reforming:<br>Regeneration by TPO of deposited carbon at 800°C and flow of 2% $O_2$ in He at 40ml/min. | |
| Syn gas catalyst.<br>(Lucki et al., 2001) | The treatment involves air oxidation, hydrogen reduction, followed by a second air oxidation. | The catalyst does not contain promoters and the treatment is applicable to either the regeneration of said spent single particle catalyst or for the initial activation of fresh catalysts. |

| Catalyst | Regeneration Procedure | Remarks |
|---|---|---|
| Ni/yttria – doped (Jenshi, Yen – Shiun, Ta – Jen, 2004) | $CO_2$ reforming at 500°C under atmospheric pressure :<br>- Regeneration of $H_2$ pre – reduction of catalyst.<br>- The gas feed pass through an $O_2$ to eliminate amount of $O_2$.<br>- The catalyst bed purge with flowing Ar at 100ml/min for 30 min to remove impurities from catalyst surface.<br>- Afterwards, a feed of $CO_2$: Ar = 25:27 at total flow rate of 100ml/min was passed to the catalyst bed to de – coke the carbon deposit. | Catalyst samples without pre – reduction by $H_2$ are not able to dissociate $CO_2$. |
| $Ni/Al_2O_3$, $Ni-Cr/Al_2O_3$ (Nichio, Quincoces, Moral, Gonzales, 2001) | Methane reforming :<br>- Regeneration with $O_2$ flow of 1% $O_2$ in $N_2$ for 2 hours at 1073K.<br>- Regeneration with $H_2$ of feed $N_2/H_2$ = 9/1 at 923K | The activity decrease in catalysts regenerated by H2 may be attributed to the permanency deactivation carbon forms and not to the active phase sintering while the regeneration in O2 removes completely the carbon forms but it allows sintering. |
| Ni – USY (Pawelec, Daza, Fierro and Anderson, 1996) | Benzene hydrogenation:<br>- Regeneration in $H_2$ at 673K<br>- Firstly with air at 673K for 1 hour and followed by the reduction in $H_2$ for 1 hour at 673K | Air / hydrogen treatment may recover the initial catalyst activity but fails to remove all carbonaceous residues from the catalyst. |

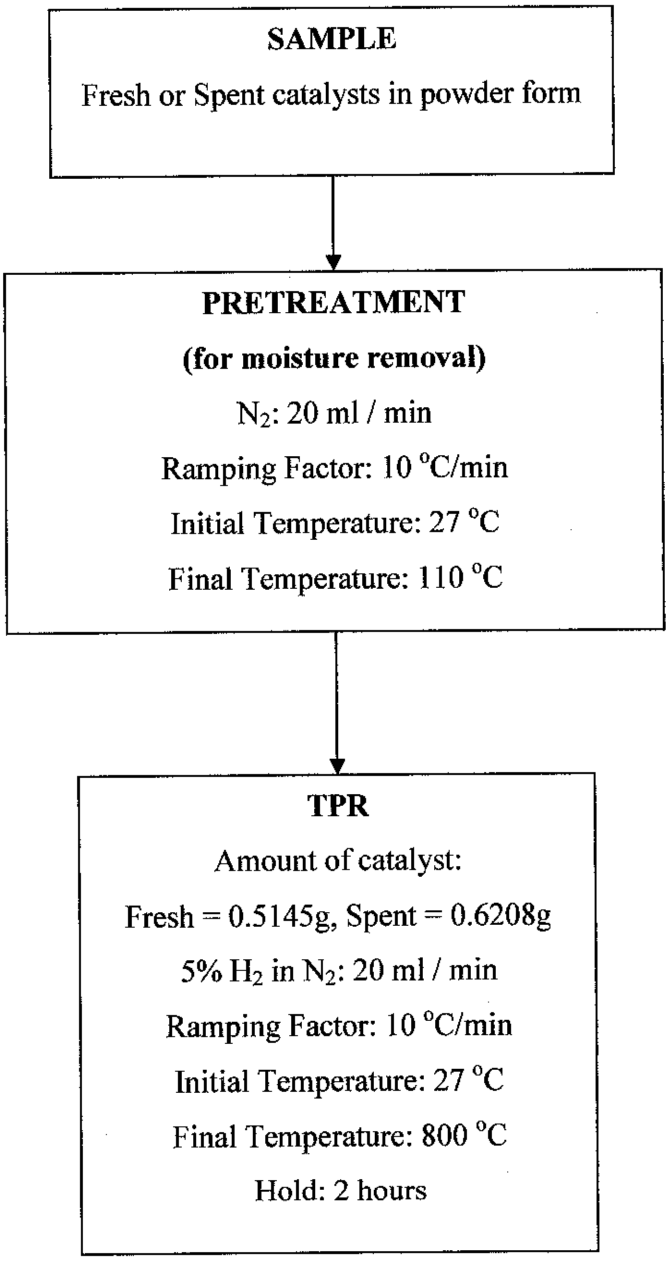
# CHAPTER 3

# METHODOLOGY / PROJECT WORK

## 3.1 Catalysts Characterization

### 3.1.1 Experimental Procedure for TPR

The TPR analysis was carried out under atmospheric pressure, in a continuous flow of hydrogen in the Thermo Finningan equipment, TPDRO 1100, which is located at Petrochemical's Laboratory. Two samples were analyzed, the fresh and spent catalyst of $NiO/MgOAl_2O_3$. The samples were reduced in a flow of $H_2$ – TPR of the catalysts was performed by heating the samples from room temperature to 800°C at a rate of 20°C/min, in a 10% $H_2/N_2$ gas flow. The weight of 0.5145g of fresh and 0.6208g of spent catalysts were placed on a quartz wool bed in an external quartz tube, positioned vertically in the oven. Each sample was pretreated in order to remove moisture before the TPR analysis. The hydrogen consumption for the reduction process was measured by using a thermal conductivity detector (TCD).



**SAMPLE**

Fresh or Spent catalysts in powder form

**PRETREATMENT**

**(for moisture removal)**

$N_2$: 20 ml / min

Ramping Factor: 10 °C/min

Initial Temperature: 27 °C

Final Temperature: 110 °C

**TPR**

Amount of catalyst:

Fresh = 0.5145g, Spent = 0.6208g

5% $H_2$ in $N_2$: 20 ml / min

Ramping Factor: 10 °C/min

Initial Temperature: 27 °C

Final Temperature: 800 °C

Hold: 2 hours

Figure 3.1.1: Flow diagram for TPR

### 3.1.2 Experimental Procedure for Regeneration of Spent Syngas Catalysts.

For this research project, two regeneration procedures have been designed. These regeneration procedures were carried out first in the oxygen atmosphere, followed by monitoring in TPR. The weight for spent catalyst used, for both procedures were 0.9733g each. The spent catalyst was placed on a quartz wool bed in an external quartz tube, positioned vertically in the oven.

For first regeneration procedure, the sample was reduced in a flow of $O_2$ where TPO of the catalyst was performed by heating the samples from room temperature to 400°C at a rate of 10°C/min, in a 10% $O_2$/He gas flow and held at 400°C for about 2 hours. With the same sample, it was then continued with TPR. The samples were reduced in a flow of $H_2$ – TPR of the catalyst was performed by heating the samples from room temperature to 800°C at a rate of 10°C/min, in a 10% $H_2/N_2$ gas flow.

The second regeneration procedure, the sample was reduced in a flow of $O_2$ where TPO of the catalyst was performed by heating the samples from room temperature to 600°C at a rate of 10°C/min, in a 10% $O_2$/He gas flow and held at 600°C for about 2 hours. With the same sample, it was then continued with TPR. The samples were reduced in a flow of $H_2$ – TPR of the catalyst was performed by heating the samples from room temperature to 800°C at a rate of 10°C/min, in a 10% $H_2/N_2$ gas flow.

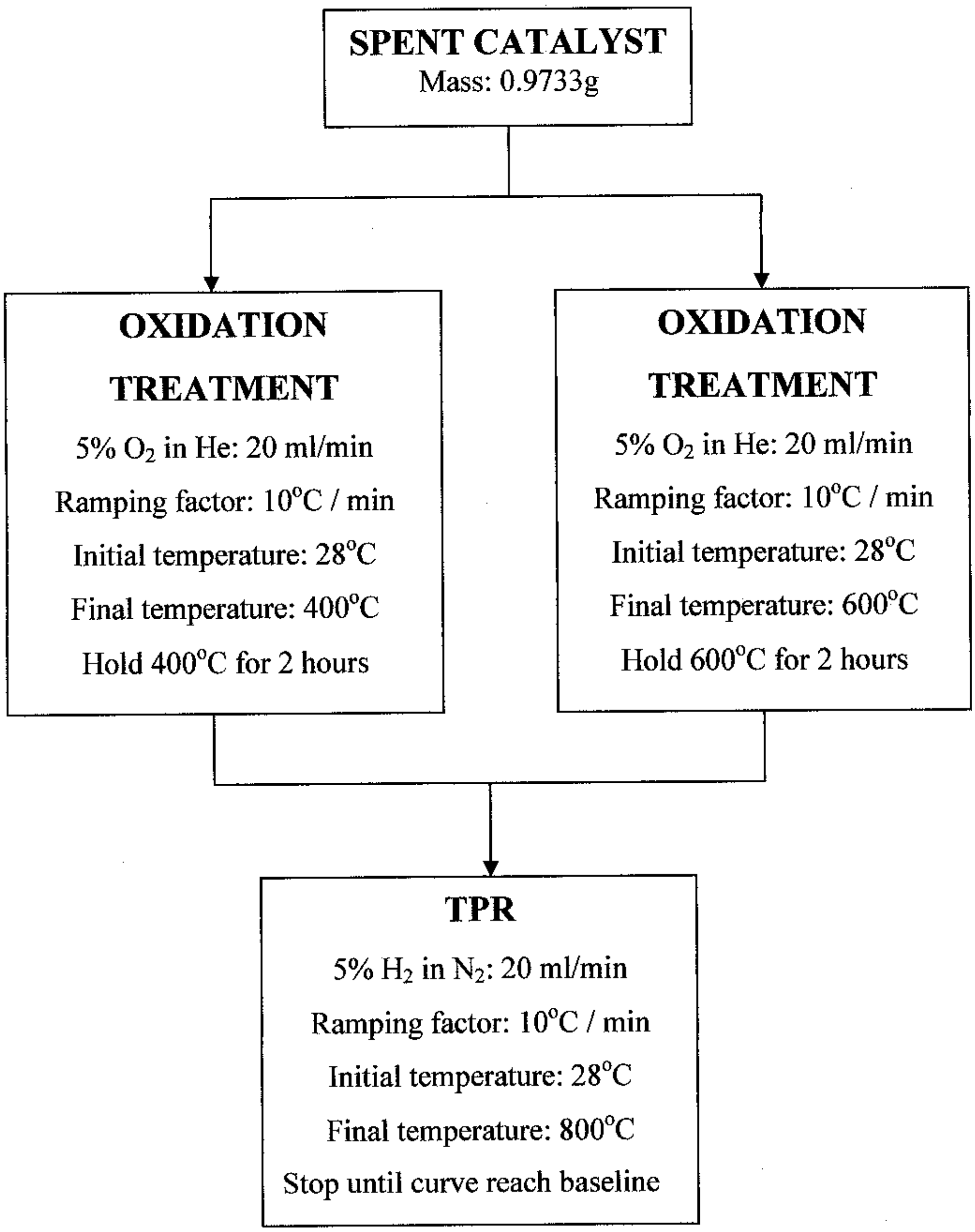


Figure 3.1.2: Flow diagram for Regeneration Procedures at 400°C and 600°C

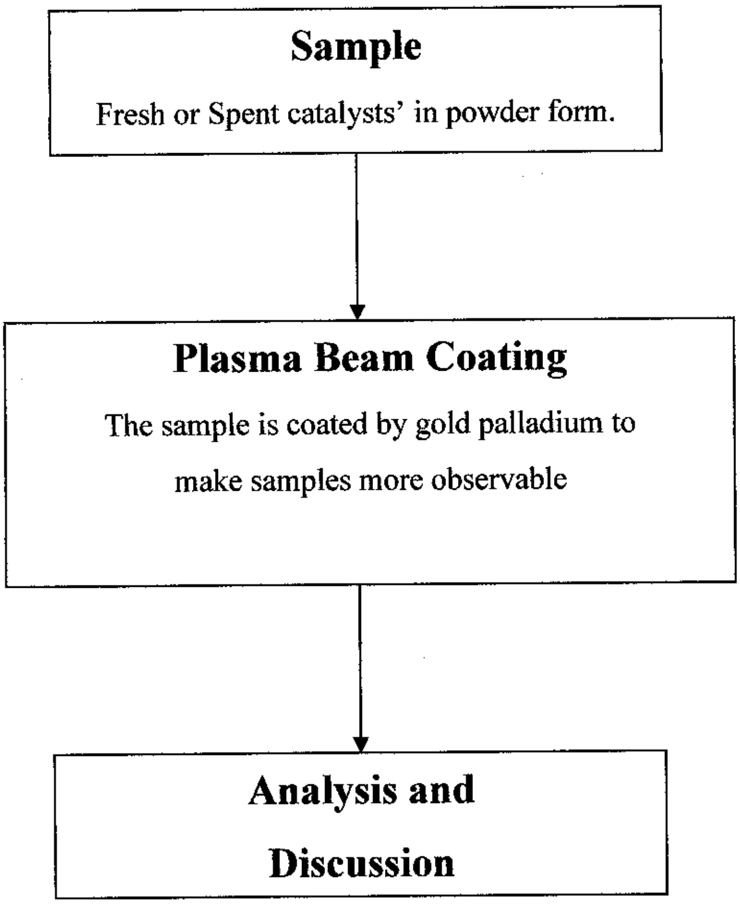
### 3.1.3 Fourier Transform Infrared Spectroscopy (FTIR)

Fresh and spent catalyst was analyzed using FTIR. It is used to determine the presence of functional group's in the catalyst. The samples to be analyzed were prepared in powder form and dry form to give more curves with sharp peaks. The samples were analyzed using FTIR by following setting:

- Range: start at 4000 $cm^{-1}$ and end at 500 $cm^{-1}$
- Scan number: 10
- Resolution: 4

Before using FTIR, the samples need to be prepared with the existence of Potassium Bromide (KBr). KBr was used to improve the scanning effect of catalyst, whereby it makes the sample to be more transparent so that the infrared can pass through the sample. Thus, it can give reading.

### 3.1.4 Experimental Procedure for EDX (Electron Dispersion X – Ray)



Fresh or Spent catalysts' in powder form.

The sample is coated by gold palladium to make samples more observable

Figure 3.1.4: Flow diagram of EDX experiment.

# CHAPTER 4

# RESULTS AND DISCUSSION

## 4.1 Temperature Programmed Reduction (TPR) Analysis

Table 4.1: TPR result for fresh and spent NiO/MgO $Al_2O_3$

| **Samples (Catalyst)** | **Reduction Temperature, °C** | | | | **Total Hydrogen Consumption μmol/g** |
|---|---|---|---|---|---|
| | **Peak 1** | **Peak 2** | **Peak 3** | **Peak 4** | |
| Fresh | 260 | 495 | 615 | - | 1445.38 |
| Spent | 200 | 450 | 520 | 800 | 71.35 |

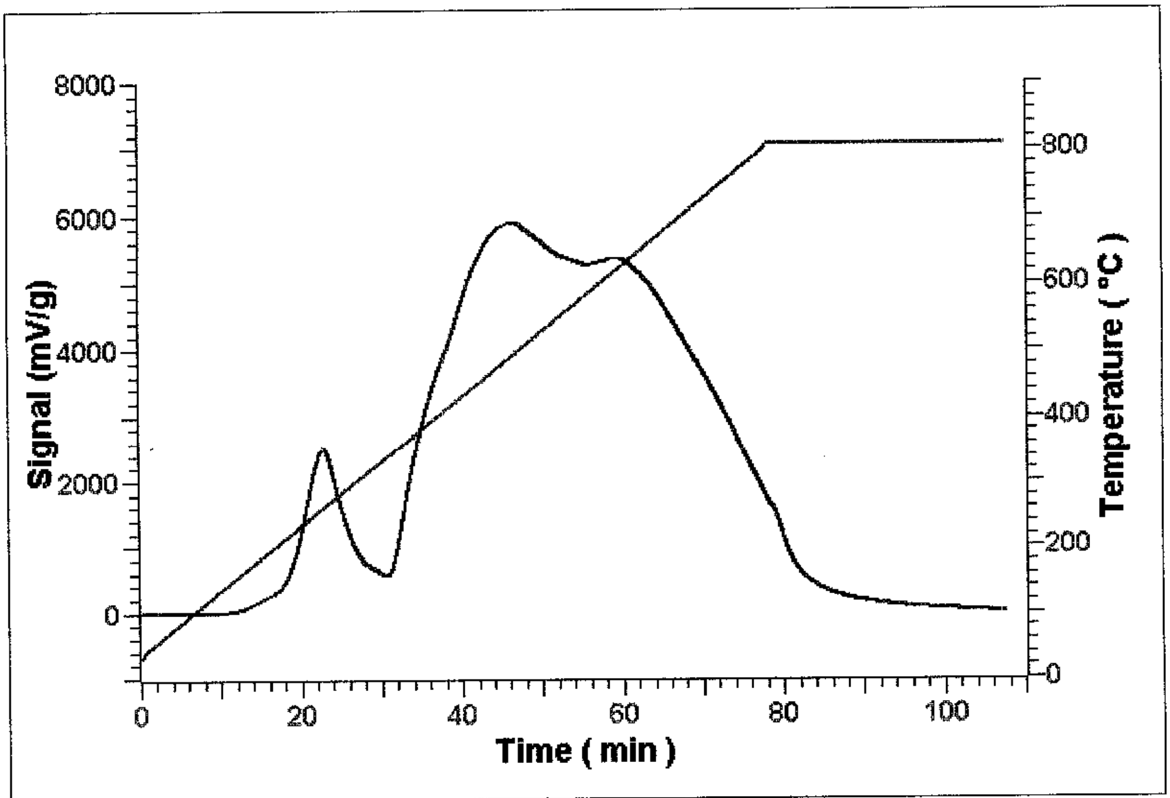


Figure 4.1: TPR profiles for fresh NiO/MgO $Al_2O_3$

From the TPR profiles shown in Figures 4.1 and 4.2, the fresh catalyst demonstrates three peaks; 260°C, 495°C and 615°C. On the other hand, the spent catalyst demonstrates four peaks at 200°C, 450°C, 520°C and 800°C. It takes about 1 hour and 20 minutes for the reduction of the fresh catalyst to complete, while for the spent catalyst, it takes about 2 hours and 20 minutes.

The first peak of the fresh catalyst, the reduction curve indicates the existence of hydrated water and this is supported by the FTIR spectrum of the sample. FTIR result, which can be referred in Figure 4.5 for fresh catalyst showed two regions; OH – stretching (3550 – 3200 $cm^{-1}$) and OH – bending (1600 – 1650 $cm^{-1}$).

It is noticed that there is a shoulder at the second peak of the TPR profiles in Figure 4.1. This shoulder is at about 410°C. This shoulder can be assigned to the hydrogen uptake of the surface nickel oxide that weakly interacts with the magnesium aluminate ($MgAl_2O_4$) supports, consistent with literature reported by Guo et al., 2004. In this literature, the shoulder of the peak is located at about 412°C.

The second peak corresponds to the reduction of NiO by consumption amount of hydrogen from the stoichiometry equation.

$$NiO + H_2 \rightarrow Ni^o + H_2O$$

For the last peak, which is at 615 °C can be assigned to the reduction of nickel oxide that are not completely integrated in the spinel structure, but have a certain degree of interaction with support. The full and complete reduction is occurring here.

As can be observed from the result, most of Ni is in the oxide form. This can be proved by determining the hydrogen consumption for fresh catalyst tabulated in Table 4.1. The area under the graph represents the amount of hydrogen consumed. Hydrogen is needed to reduce NiO into nickel metal. Since there is more NiO in the fresh catalyst, more hydrogen is consumed during reduction.

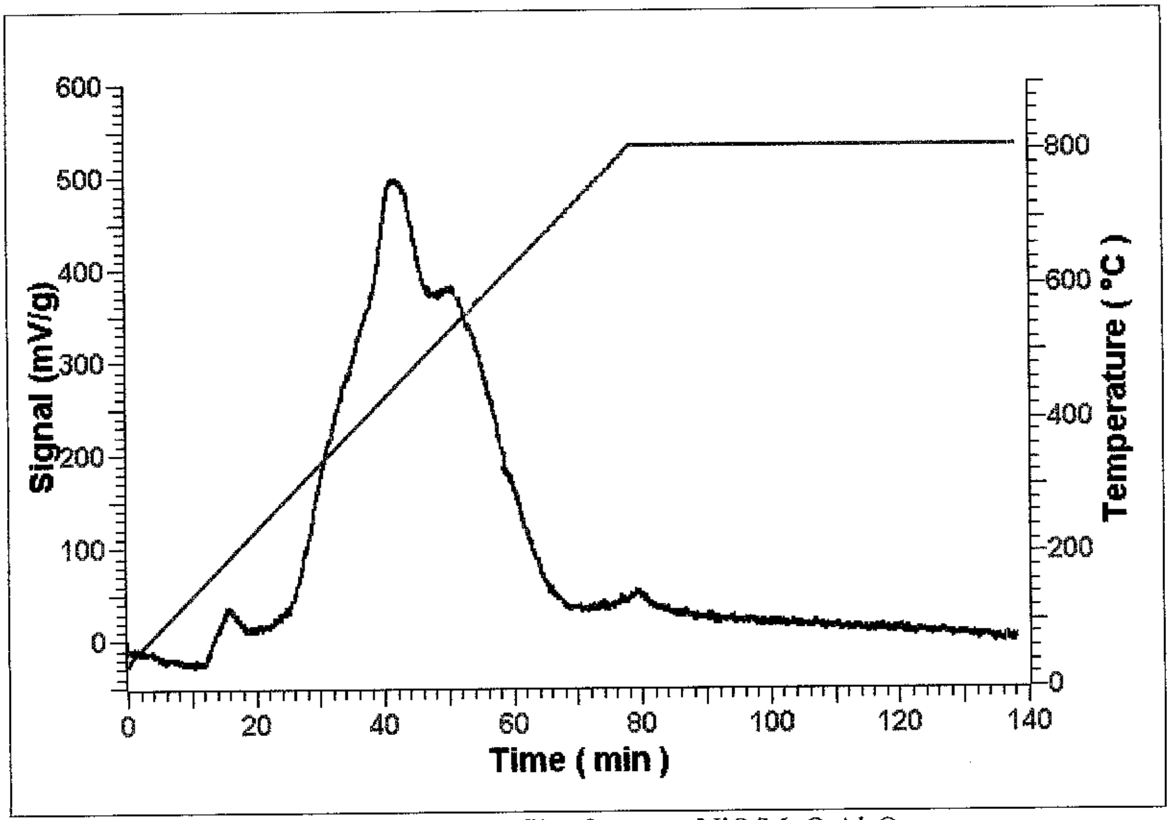


Figure 4.2: TPR profiles for spent NiO/MgO $Al_2O_3$

A reduction of spent catalyst started at 200°C, which is the lowest peak of the reduction process. From FTIR analysis in Figure 4.6, OH – curve is observed. This can be concluded that, hydrated water exists in the spent catalyst.

It is noticed that, there is a shoulder at the second peak (450°C). This shoulder may be assigned to the hydrogen uptake of the surface nickel oxide that weakly interacts with the $MgAl_2O_4$ support. A second peak indicates the reduction of NiO in mass. This peak also indicates that the NiO particle is large. These leads to easy reduction of NiO to become metallic nickel (Guo et al., 2004).

Choudhary et al., 1998, have proposed that, there is a minor phase of $MgAl_2O_4$ resulting from a solid – solid reaction between MgO and $Al_2O_3$. This proposal consistent with literature reported by Guo et al., 2004, where there is formation of $MgAl_2O_4$ spinel, an outer layer phase on the surface of $Al_2O_3$.

The $MgAl_2O_4$ spinel layer in Ni/MgO $Al_2O_3$ can effectively suppress the phase transformation to form Ni $Al_2O_3$ spinel phase (Guo et al., 2004), which is difficult to reduce (Choudhary et al., 1998).

From all these literatures, the third peak at 530°C represents the reduction of NiO that is weakly interacts with $MgAl_2O_4$ support.

As reported by Guo et al., 2004, a high temperature above 800°C was required to reduce the non – stoichiometric surface $Ni/Al_2O_3$ species. From the TPR result of the spent catalyst, the forth reduction peak is occurred approximately at 800°C. Although there is formation of $MgAl_2O_4$, this formation does not fully prevent the chemical reaction between nickel and alumina, producing of catalytically inactive $Ni/Al_2O_3$ spinel phase, which is difficult to reduce (Choudhary et al., 1998).

Therefore, the forth peak as mentioned indicated the reduction of NiO that is having an interaction with the $Ni/Al_2O_3$ spinel phase. Since this spinel phase is difficult to reduce, this reduction take place at extremely high temperature.

It is observed that, the total hydrogen consumption for spent catalyst is much lower than fresh, which is 71.35 μmol/g. Small amount of hydrogen consumed during reduction, indicates that the percentage of NiO is lower and the percentage of Ni metallic is higher. Therefore, smaller amount of NiO that needs to be reduced. This also indicates that, there is more nickel in the metallic form in the spent compare to nickel present in oxide form.

As demonstrated by the TPR studies, the larger the particles of supported nickel oxide, the easier they could be reduced to metallic form, considering the presence of metal – support interaction (Guo et al., 2004). In this case, the interaction is between nickel and alumina. Guo et al., 2004, also reported that, when the size of nickel oxide particle is large, the reduction temperature become low.

From the result, the reduction peak is in order; start with the lowest reduction temperature (200 °C) and the last peak at the highest reduction temperature (800 °C). This result is consistent with literature reported by Guo et al., 2004, that is the reduction of NiO is started with the largest particle of supported nickel oxide and ended with the smallest particle of supported nickel oxide.

## 4.2 Regeneration Analysis in Oxygen Atmosphere

### 4.2.1 Regeneration at 400°C in Oxygen Atmosphere

Table 4.2: TPR result for regeneration at 400°C

| **Regeneration at 400°C in Oxygen Atmosphere** | | |
|---|---|---|
| **Peak** | **Reduction Temperature, °C** | **Total Hydrogen Consumption μmol/g** |
| 1 | 460 | 90.71 |
| 2 | 520 | |
| 3 | 800 | |

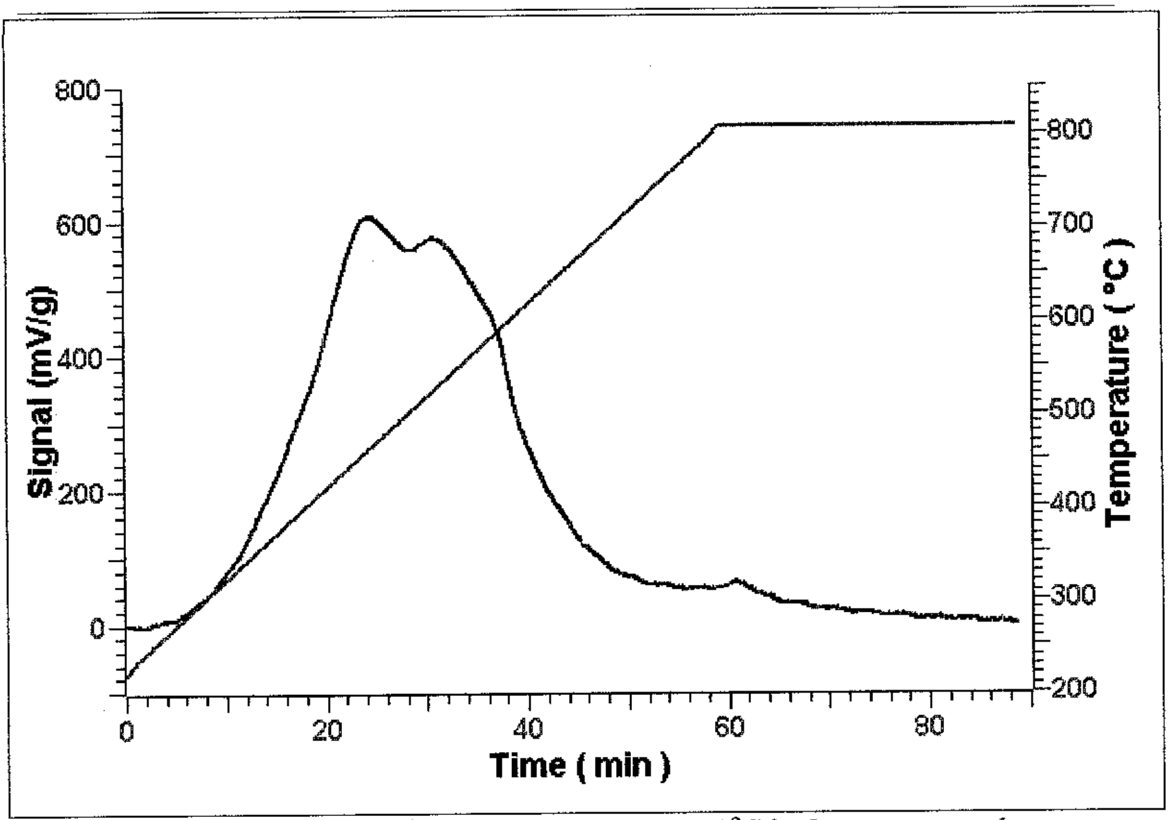


Figure 4.3: TPR profiles for Regeneration at 400°C in Oxygen atmosphere

In general, air treatment may recover the initial catalyst activity but fails to remove the carbonaceous residues from the catalyst. For the first trial of regeneration in oxygen atmosphere, oxidation at 400°C for two hours and followed by TPR until 800°C. Based on Figure 4.3, three peaks are observed; 460, 520 and 800°C.

Total hydrogen consumption is 90.71μmol/g. Small amount of hydrogen consumed during reduction indicates that the percentage of NiO is lower and the percentage of Ni metallic is higher.

TPR profiles for regeneration at 400°C showed a closer resemblance to the TPR profiles of fresh catalyst in Figure 4.1. The regeneration profiles also are shifted to the left. The absence of the first peak at 260°C is suspected due to the high temperature.

### 4.2.2 Regeneration at 600°C in Oxygen Atmosphere

Table 4.3: TPR result for regeneration at 600°C

| **Regeneration at 600°C in Oxygen Atmosphere** | | |
|---|---|---|
| **Peak** | **Reduction Temperature, °C** | **Total Hydrogen Consumption µmol/g** |
| 1 | 380 | 80.63 |
| 2 | 610 | |
| 3 | 730 | |
| 4 | 800 | |

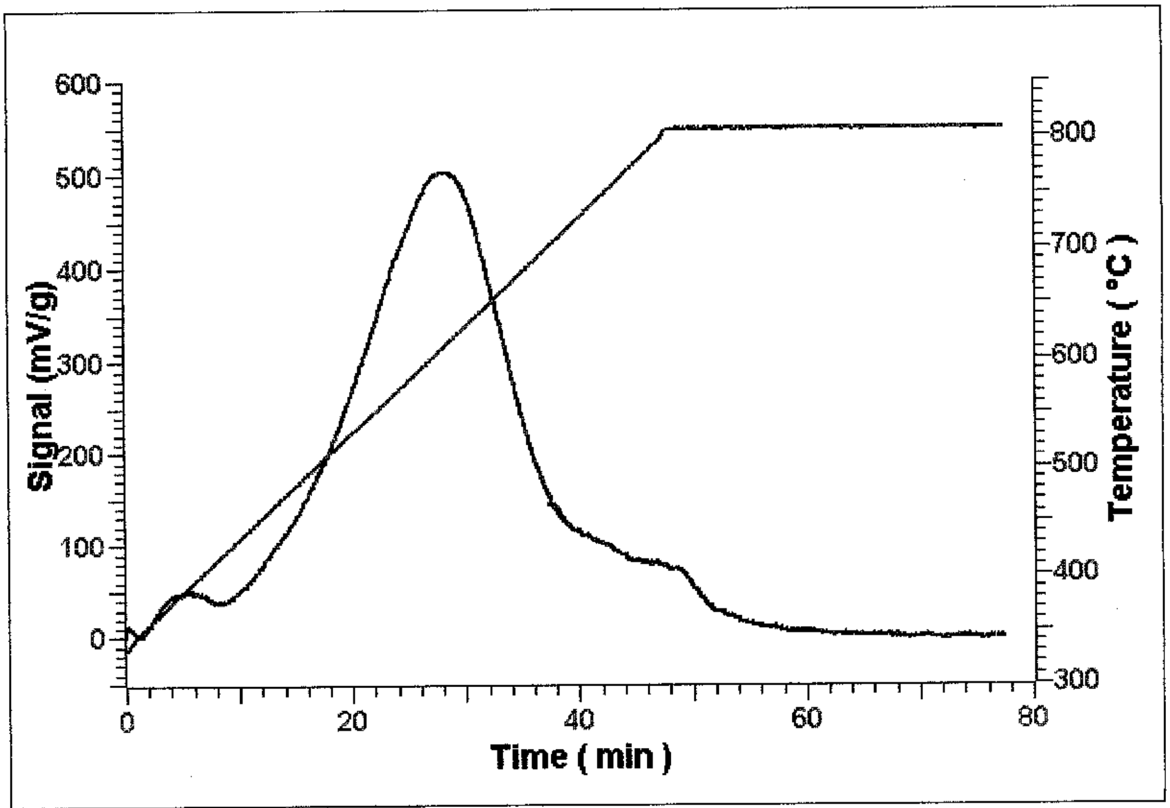


Figure 4.4: TPR profiles for Regeneration at 600°C in Oxygen atmosphere

For the second trial of regeneration in oxygen atmosphere, oxidation at 600°C for two hours and followed by TPR until 800°C. Based on Figure 4.4, four peaks are observed; 380, 610, 730 and 800°C.

Total hydrogen consumption is 80.63 µmol/g lower than for regeneration at 400°C. Small amount of hydrogen consumed during reduction indicates that the percentage of NiO is lower and the percentage of Ni metallic is higher. Therefore, smaller amount of NiO that needs to be reduced. This also indicates that, there is more nickel in the metallic form in the regenerated catalyst than oxide form.

By comparing the TPR profile for regeneration at 600°C with the TPR of fresh catalyst in Figure 4.1, regeneration at 600°C seemed not to produce a regenerated catalyst with close resemblance to the fresh catalyst. The regeneration at 600°C TPR profiles seemed not close to either TPR for fresh catalyst (Figure 4.1) or spent catalyst (Figure 4.2).

## 4.3 FTIR (Fourier Transform Spectroscopy Spectrum) analysis.

Table 4.4: FTIR result for fresh and spent NiO / MgO $Al_2O_3$

| Samples | Region ($cm^{-1}$) | Functional Group |
|---|---|---|
| Fresh | 3550 – 3200 | OH – stretching |
| | 1600 – 1650 | OH – bending |
| | 1350 – 1400 | $NO_3$ group |
| Spent | 3550 – 3200 | OH – stretching |
| | 1600 – 1650 | OH – bending |

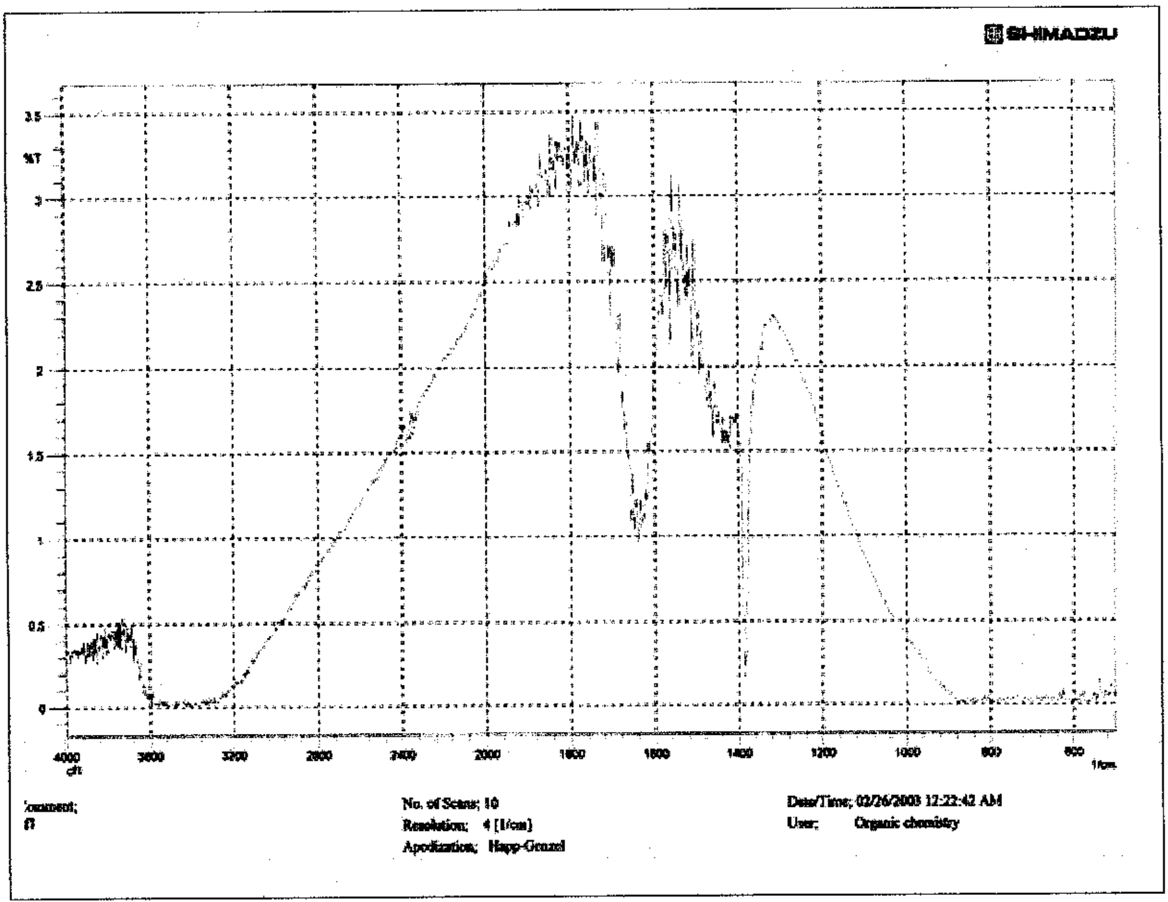


Figure 4.5: FTIR spectra of fresh catalysts

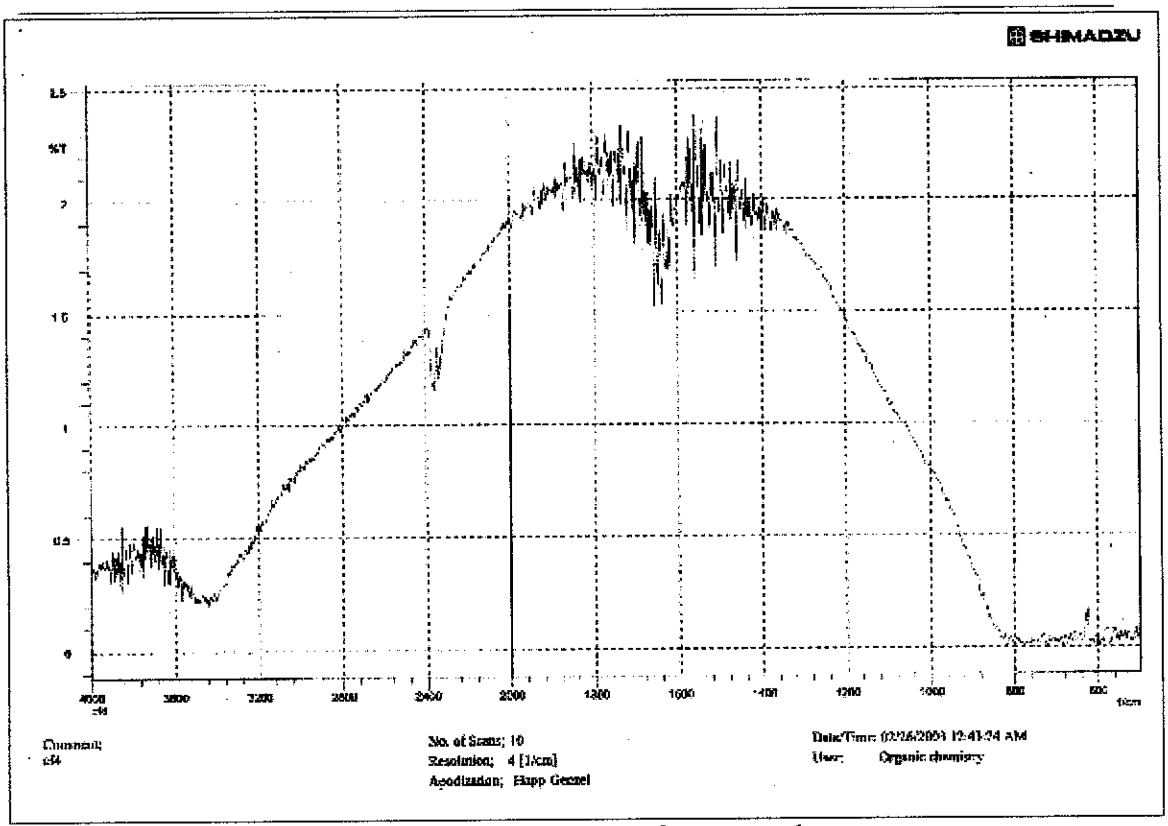


Figure 4.6: FTIR spectra of spent catalysts

Figures 4.5 and 4.6 are FTIR spectra of fresh and spent catalysts. The samples contain some moisture and some broader bands caused by the hydrogen bonding.

Absorption bands in the range of 1000 – 4000 cm$^{-1}$ due to functional group such as –OH, C=O, N-H and $CH_3$. These peaks are characterized by the specific bonds in order to identify the functional group of samples. They may be a characteristic of molecular symmetry, or combination bands arising from multiple bands deforming simultaneously.

Figure 4.5 represents the FTIR spectrum of fresh catalyst. The band observed at the range of 3200 – 3550 cm$^{-1}$ indicates the existence of –OH stretching, might be from moisture. The band observed at the range of 1600 – 1650 cm$^{-1}$ is due to –OH bending.

It is noticed that, there is a band at the range of 1350 – 1400 $cm^{-1}$. This band indicates the presence of $NO_3$ group. The existence of this group is believed due to the preparation of the catalysts by the wet impregnation method, using nitrate salt as precursor. (Guo et al., 2004)

Figure 4.6 represents the FTIR spectrum of spent catalyst. The same band observed at the range of 3200 – 3550 $cm^{-1}$ indicates the existence of –OH stretching, might be from moisture. The band observed at the range of 1600 – 1650 $cm^{-1}$ is due to –OH bending.

It was expected that the hydrocarbon band ($-CH_3$, $-CH_2$, -CH) will appear in the spectrum of the spent catalyst. If there is the presence of hydrocarbon, there will be adsorption band observed at the range of 2800 – 3500 $cm^{-1}$ wave number. However, no such bands were identified indicating the absence of the hydrocarbon species. However, the notion that graphite or polymerized coke may be present in the spent catalyst could not be ruled out.

## 4.4 Electron Dispersion X – Ray (EDX) analysis.

Table 4.5: Nickel content in weight% for fresh and spent syngas catalyst

| **Spot** / **Samples** | **1 (wt%)** | **2 (wt%)** | **3 (wt%)** | **Average (wt%)** |
|---|---|---|---|---|
| **Fresh** | 7.8 | 11.69 | 15.25 | **11.58** |
| **Spent** | 8.49 | 4.72 | 4.02 | **5.74** |

As tabulated in Table 4.5, the Ni content is reduced for the spent catalyst. Nickel content observed by EDX in fresh catalyst is 11.58wt%, which is in the range (7 – 13wt %), while for spent catalysts, nickel content is 5.74wt %. The difference of nickel content between fresh and spent catalyst is 5.84wt %.

This results show that there is some loss of Ni content after the reaction. The loss is due to sintering. Sintering is the loss of metal or metal oxide surface area due to growth of metal or metal oxide crystallites; this growth may occur by metal atom migration, crystallites migration or vaporization. Guo et al., 2004, also reported that one possible reason for deactivation of $NiO/MgOAl_2O_3$ could be loss of $Ni^0$ active area due to severe sintering of metal particles.

Sintering process generally takes place at higher reaction temperature that is above 500°C and are generally accelerated by the presence of water vapor.(Bartholomew, 1997). Thus, the operating condition of steam reforming enhances the sintering process to occur. Secondary steam reforming operates at 960°C in the presence of steam.

# CHAPTER 5

# CONCLUSION AND RECOMMENDATION

## 5.1 Conclusion

From the project, the characteristic of the catalyst can be determined using TPDRO equipment. This will also give the analysis of the catalyst performance and design an appropriate regeneration procedure of the spent catalyst.

In the temperature programmed reduction analysis (TPR), sample's characteristic such as temperature at which the reduction takes place and the amount of hydrogen consumed have been observed. From the TPR result, the amount of hydrogen consumed for fresh catalyst is higher than for spent catalyst. This indicates that there are more nickel in the oxide form exists in fresh catalyst than in the spent catalyst.

From TPR analysis also, it is noticed that the existence of metal – support interaction; Ni – $Al_2O_3$, which is difficult to reduce. This can be proved by the existence of reduction peak temperature at 800°C.

Two sets of regeneration procedures have been design; regeneration at 400°C in oxygen atmosphere and at 600°C in oxygen atmosphere. None of these two designs showed similar TPR to TPR of the fresh sample. However, the lower regeneration temperature seemed to produce a regenerated catalyst with close resemblance to the fresh catalyst.

From FTIR analysis, the functional group of fresh and spent catalyst is identified. The functional group present in fresh catalyst are; –OH bending and stretching, and nitrate group. The presence of nitrate is believed due to the preparation of catalyst, where nitrate salt is used as precursor. For spent catalysts, only –OH bending and stretching identified. No hydrocarbon group was detected.

Loss in nickel content is identified in spent catalysts. Nickel content observed by EDX in fresh catalyst is 11.58wt%, which is in the range (7 – 13wt %). While for spent catalysts, nickel content is 5.74wt %. The difference of nickel content between fresh and spent catalyst is 5.84wt %.

The loss is due to sintering. Sintering rate increase exponentially with temperature and water vapor. Sintering will increase the rates of metal surface area loss.

## 5.2 Suggested future work for continuation project

The recommended future works that can be considered to improve results achieve and determine the research project in detail:

1) Conduct TPO experiments for fresh and spent syngas catalysts.
2) For TPR and TPO experiments, it is recommended to connect to a mass spectrometer to determine the species present accurately, precisely and immediately.
3) For regeneration section, it is recommended to conduct regeneration at higher than 800°C and lower than 400°C in oxygen atmosphere.
4) Take more than five spots for more accurate elemental determination in EDX experiment.
5) Other characterization techniques is recommended to conduct such as:

-AAS (Atomic Absorption spectrometry), to determine nickel composition present in catalysts.

-TGA (Thermogravimetric Analysis), to determine weight loss of spent and fresh catalysts.

-CHNS (carbon, hydrogen, nitrogen, sulfur), to determine the existence of carbon, hydrogen, nitrogen and sulfur compound in catalysts.

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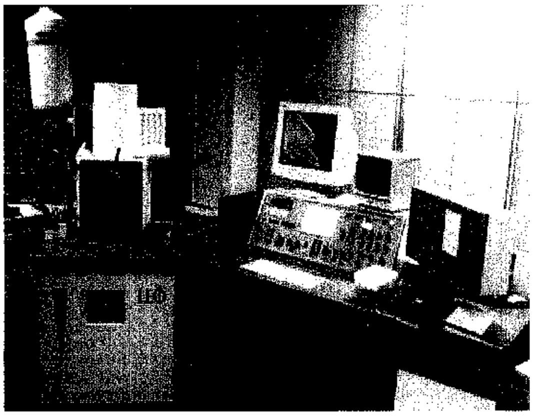
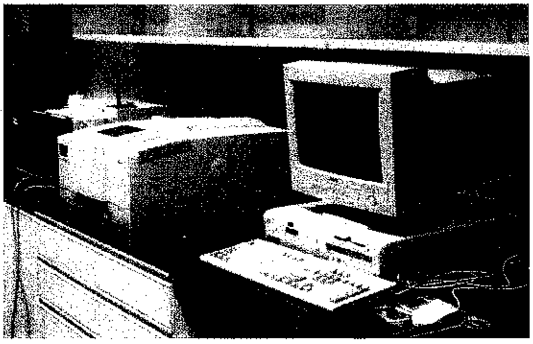
# APPENDICES

1) List of equipment used:

| Name | Location | Function |
|---|---|---|
| 1. Temperature Programme Desorption Reduction & Oxidation (TPDRO) | 03-02-03<br> | Catalysyt characterization at High T and P |
| 2. Scanning Electron Microscope (SEM) | 17-00-10<br> | Scanning image of sample surface structure and EDX<br>Look at morphology of material and identify and quantify components in surface layer |
| 3. Fourier Transform Infra-Red (FTIR) | 04-00-06<br> | Infrared transmittance or absorbance of a sample obtained as a functional group determination |

2) EDX results

Fresh Catalyst

First spot :

Magnification = 3000x

| Element | App<br>Conc. | Intensity<br>Corrn. | Weight% | Weight%<br>Sigma | Atomic% |
|---|---|---|---|---|---|
| O K | 148.09 | 1.0129 | 51.06 | 1.37 | 65.25 |
| Mg K | 16.37 | 0.5492 | 10.41 | 0.71 | 8.76 |
| Al K | 47.94 | 0.5453 | 30.70 | 1.01 | 23.27 |
| Ni K | 19.46 | 0.8681 | 7.83 | 0.52 | 2.73 |
| | | | | | |
| Totals | | | 100.00 | | |

Second spot :

Magnification = 5000x

| Element | App<br>Conc. | Intensity<br>Corrn. | Weight% | Weight%<br>Sigma | Atomic% |
|---|---|---|---|---|---|
| O K | 40.21 | 1.0364 | 50.25 | 2.65 | 65.52 |
| Mg K | 4.14 | 0.5003 | 10.70 | 1.51 | 9.18 |
| Al K | 10.75 | 0.5081 | 27.35 | 1.83 | 21.15 |
| Ni K | 7.88 | 0.8724 | 11.69 | 1.31 | 4.15 |
| | | | | | |
| Totals | | | 100.00 | | |

Third spot :

Magnification = 8000x

| Element | App<br>Conc. | Intensity<br>Corrn. | Weight% | Weight%<br>Sigma | Atomic% |
|---|---|---|---|---|---|
| O K | 57.34 | 0.9243 | 41.00 | 2.27 | 57.04 |
| Mg K | 9.04 | 0.5014 | 11.92 | 1.12 | 10.91 |
| Al K | 23.98 | 0.4976 | 31.84 | 1.52 | 26.26 |
| Ni K | 20.34 | 0.8817 | 15.25 | 1.04 | 5.78 |
| | | | | | |
| Totals | | | 100.00 | | |

Spent Catalyst

First spot :

Magnification = 1000x

| Element | App Conc. | Intensity Corrn. | Weight% | Weight% Sigma | Atomic% |
|---|---|---|---|---|---|
| O K | 8.75 | 0.9923 | 48.63 | 2.60 | 63.00 |
| Mg K | 1.27 | 0.5528 | 12.62 | 1.37 | 10.76 |
| Al K | 2.89 | 0.5252 | 30.26 | 1.82 | 23.25 |
| Ni K | 1.34 | 0.8698 | 8.49 | 1.04 | 3.00 |
| | | | | | |
| Totals | | | 100.00 | | |

Second spot :

Magnification = 5000x

| Element | App Conc. | Intensity Corrn. | Weight% | Weight% Sigma | Atomic% |
|---|---|---|---|---|---|
| O K | 88.14 | 0.9550 | 47.12 | 1.86 | 60.81 |
| Mg K | 16.34 | 0.6091 | 13.70 | 0.92 | 11.63 |
| Al K | 35.76 | 0.5486 | 33.28 | 1.35 | 25.47 |
| Fe K | 2.02 | 0.8732 | 1.18 | 0.31 | 0.44 |
| Ni K | 8.00 | 0.8654 | 4.72 | 0.57 | 1.66 |
| | | | | | |
| Totals | | | 100.00 | | |

Third spot :

Magnification = 8000x

| Element | App Conc. | Intensity Corrn. | Weight% | Weight% Sigma | Atomic% |
|---|---|---|---|---|---|
| C K | 3.49 | 0.3877 | 30.98 | 6.37 | 41.85 |
| O K | 6.58 | 0.5366 | 42.34 | 4.76 | 42.94 |
| Mg K | 1.22 | 0.5800 | 7.24 | 1.05 | 4.83 |
| Al K | 2.68 | 0.6014 | 15.41 | 1.73 | 9.27 |
| Ni K | 0.98 | 0.8396 | 4.02 | 0.71 | 1.11 |
| | | | | | |
| Totals | | | 100.00 | | |