TEMPERATURE-PROGRAMMED CHARACTERIZATION OF

SPENT SYNGAS CATALYST

(NiO/CaO)

By

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

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the

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in partial fulfillment of the requirement for the

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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 acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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NIK ZARINA SURYANA BT NIK KHAMSANI

ABSTRACT

This research project is conducted to characterize the fresh and spent catalyst of NiO/CaO using temperature programmed. The characterization techniques used are Temperature Programmed Reduction (TPR) and Temperature Programmed Oxidation (TPO). Characterization of catalyst is important in order to determine the catalyst properties. The author has analyzed several methods used such as TPR, TPO, FTIR and CHNS, which had led to significant findings in this area of study. TPR analysis is used to determine the temperature at which reduction take place in the species. From this, it can also be observed the amount of hydrogen consumption and determine the other contaminant species reduced especially for spent catalyst. For the fresh catalyst, the nickel species are reduced at 410 °C and 680 °C, while for the spent catalyst, it is reduced at 400 °C and 640 °C. There are two NiO particles size distribution exists which are lower reduction temperature particles range for smaller size and higher reduction temperature range for bigger size.

TPO analysis is used to determine the temperature at which oxidation take place in the catalysts. From both two analysis, TPR and TPO, it is necessary to determine the regeneration method, which can improve the catalyst performance similar to fresh catalyst. CHNS is used in order to determine the amount of carbon and hydrogen contained in the catalyst. This project concluded that high carbonate content in the spent catalyst. FTIR is one of the methods to identify the functional group present in the catalyst. From FTIR plot, it is observed that carbonate and –OH present in the spent catalyst, meanwhile only –OH present in the fresh catalyst.

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INTRODUCTION

1.1 Background of Study

1.1.1 Syngas production from reforming

Hydrocarbons are the most important raw materials of the production hydrogen and synthesis gas. Hydrogen is a fundamental feedstock for refining processes such as hydrotreating, hydrocracking and also some petrochemical processes such as methanol, and ammonia synthesis. (Source: The British Sulfur Corp. LTD. 1992; Twigg, 1997). This gas can be directly burnt in an internal combustion engine or can also be electro chemically converted to electricity in a fuel-cell system. (Source: Dias and Assaf, 2004).

Many important chemical processes require synthesis gas, also called syngas. Syngas is a mixture of hydrogen and carbon monoxide (CO) produced by steam, carbon dioxide, autothermal reforming or partial oxidation of natural gas (methane).

The reforming of methane with steam is a widely employed method for hydrogen production in the world. Syngas produced from steam reforming gives higher ratio of H_2/CO (3:1), which can be determined from the equation below. Energy is supplied to drive this endothermic reaction by heating the reactor externally.

$$CH_4 + H_2O \rightarrow CO + 3\,H_2$$
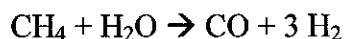
The steam to carbon ratio in the feed gas usually conducts at condition range of 1.9-9.0. This is because the coke formation, which destroys the catalyst structure and kills its activity, is thermodynamically favored at 637°C under atmospheric pressure and a steam to carbon ratio less than 1.4. (Source: Van Hook, 1980). Therefore, the industrial of steam reforming is usually run under a steam-to-carbon ratio of 1.4 or higher in order to maintain the catalyst activity and favor the reverse reaction. Alkali is added to nickel surface, primarily K_2O or CaO, which is able to increase the water adsorption.

Another way of making synthesis gas from methane (CH_4) is from carbon dioxide (CO_2). Since CO_2 are the green house gasses and they contribute to world wide environmental issue which is global warming, and their amount should be suppressed. Therefore, the CO_2 reforming of CH_4 is an appropriate reaction to convert these harmful gases into syngas, which is a useful feedstock for chemical industries.

$$CH_4 + CO_2 \rightarrow 2CO + 2 H_2$$

Syngas also can be produced by direct partial oxidation which yield H_2/CO ratio 2:1 as shown below. This reaction is exothermic and the H_2/CO ratio of the product is more desirable for most petrochemical synthesis. This reaction can be also carried out without any catalyst.

$$CH_4 + O_2 \rightarrow CO + 2 H_2$$

Commercially, this CH_4 reforming uses the nickel catalyst supported by 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, which lead to catalyst deactivation.

Larger crystallites of nickel promote coke formation causing catalyst deactivation. Therefore, the stability of the catalysts under methane reforming condition maybe optimized by using catalysts containing low loadings of nickel. (Source: Delmon and Froment, 1994).

Although the supported noble metals such as Rhenium, Platinum, Iridium, pyrochlore and perovskite oxides-containing noble metals have possessed excellent resistance to coke deposition, their uses are limited by their extremely high cost. (Source: Claridge, Tsang, York, Ashcroff Battle, 1993). Therefore, it is desirable to develop catalyst with nickel based that has a good resistance to coke.

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1.1.2 Catalyst deactivation

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

Poisoning of the catalyst occurs by the adsorption of impurities in the feed on the specific catalyst sites. The most common cause for poisoning is the chemisorptions of gaseous species on the active sites of catalyst, such as nitrogen and sulfur. Pore collapse is one of the catalyst deactivation cause by the sintering of the catalyst and support.

The coke deposition during steam reforming is formed by the methane itself and carbon monoxide, which can be determined by the simplified mechanism below. The catalyst needs 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. Catalysts 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 add to the catalyst in order to enhance regeneration. Thus, Andrew has suggested that alkali move across the nickel surface to accelerate the removal rate of carbon residues. (Source: Andrew, 1969).

From Nichio studies, the results of Ni-Cr/Al2O3 catalyst sample regenerated by hydrogen and oxidation after partial oxidation and methane reforming process are similar. The sample regenerated with oxygen removes completely carbon formation but allow sintering, meanwhile the sample regenerated by hydrogen decrease in activity since it is deactivated by the carbon formed on the catalyst. (Source: Nichio and Quincoces, 2001).

The regeneration procedure was carried out with oxygen flow of 1% O_2 in N_2 for 2 hours at 1073K. For regeneration with H_2, feed of N_2/H_2 = 9/1 was carried out at 923K. The regeneration by hydrogen does not recover the initial catalytic property and nickel catalyst showed a lower remnant magnetism, which would indicate an increase in the dispersion of metallic phase. A contrary result for sample regenerated in oxygen, which shows that the particle sizes increase by sintering. (Source: Nichio and Quincoces, 2001).

The addition of air to the feed in the authothermal reforming decreased drastically the amount of carbon formed on the catalyst, approaching zero at an O_2/CH_4 ratio of 0.13, which indicates that at higher $O_2:CH_4$ ratios, with a H_2O/CH_4 ratio of 0.25, carbon deposition would not occur. This also provides strong evidence that this process will reliable avoid coke formation at higher contents of H_2O and in the feed. (Source: Dias, Jose and Assaf, 2004).

Meanwhile for steam reforming process, it 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 design an appropriate regeneration procedure with optimum condition to remove coke deposition effectively based on the temperature-programmed characterization of fresh and spent catalyst.

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1.2   Problem Statement

1.2.1   Problem identification

The catalyst surface becomes 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.

A significant difficulty with the practical use of Ni as catalyst for steam reforming is the formation of the surface carbon. Coke deposition has the biggest impact on the process operation mainly because of an increase in pressure drop and decrease of the heat transfer efficiency. The type of coke deposited is related to the C: H ratio which indirectly determines the ease of removal during regeneration.

By regenerating the spent catalyst, it will offer significant means of removing the amount of coke deposited and solving the disposal problem of spent catalyst.

1.2.2   Significant of the project

This project involves characterization of the spent and fresh catalysts for steam reforming using temperature programmed technique and some instrumental methods to study the catalysts' characteristic and catalytic performance. The spent catalyst has been deactivated after certain period of operation usually caused by coke deposition and sintering. Therefore, the information gathered on the spent and fresh catalyst is used to design an appropriate regeneration procedure for spent catalyst.

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1.3 Objective and scope of study

The objectives of this study are:

1. To determine the physical properties of fresh and spent catalyst by using Temperature Programmed Reduction, Oxidation (TPDRO).

2. To design a regeneration procedure for the spent catalyst.

The scope includes a thorough literature research on nickel based catalyst, steam reforming process, TPDRO equipment, catalyst deactivation such as coke deposition, regeneration procedure from various sources of journals through internet and books. The experiments were conducted using the TPDRO equipment to characterize the physical properties of catalysts and design an appropriate regeneration procedure based on some literatures.

CHAPTER 2

LITERATURE REVIEW

2.1 Syngas production from reforming

The conversion of hydrocarbon fuels to H_2 can be carried out by several processes, including steam reforming, dry reforming, partial oxidation, and autothermal reforming. Steam reforming involves the reaction of steam with the fuel in the presence of a catalyst to produce H_2 and CO. Since steam reforming is endothermic, some fuel must be burned and the heat is transferred to the reformer by heat exchangers. The simplified process involved in hydrogen steam reforming plant is shown in Figure 2.1.
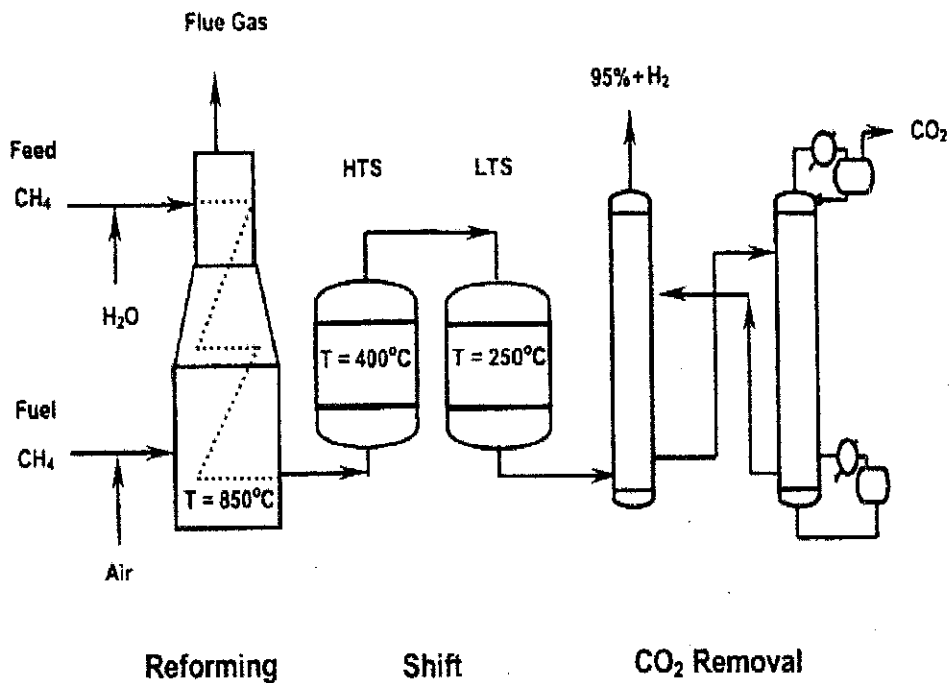
Figure 2.1: Simplified flow diagram of the conventional steam methane reforming

Sygas produced from carbon dioxide and methane is called dry reforming. It is practical for the industrial interest since it gives low CO/H_2 ratio. Partial oxidation involves the reaction of oxygen with fuel to produce H_2 and CO when the oxygen-to-fuel ratio is less than the required for total combustion. Autothermal reforming involves the reaction of oxygen, steam, and fuel to produce H_2 and CO_2, and can be viewed as a combination of partial oxidation and steam reforming.

2.2   NiO/CaO catalyst

In general, methane reforming is catalyzed by group VIII transition metals, such as nickel and noble metals; rhodium, iridium and ruthenium. The coke formation can be reduced by using noble metal catalysts such as ruthenium and rhodium but they are more expensive. Catalysts based on noble metals are less sensitive to coking compared to nickel based catalyst. Nickel is available at a low price and highly active for this reaction, at least at initial stage, but losses its activity rapidly by carbon deposition. Although noble metals have been proved to be less sensitive for carbon deposition on the surface it is important to develop Ni-based catalyst because of its low cost and high availability of nickel. (Source: Tang and Lin, 1998)

The components of catalyst are catalytic active phase, supports, binders and promoters. (Source: Kirk Othmer, p.357). Typically major component is support, an inexpensive metal oxide such as alumina, MgO or CaO. The catalytically active components are often expensive. Therefore, it is dispersed into small particles on the interior surface of porous support to maximize their utilization. Addition of promoters into catalyst is the simplest and cheapest way to improve their quality. Raw materials such as limestone or dolomite for CaO based absorbent are plentiful and inexpensive.

CaO-based absorbent is usually being used because the excellent absorption capacity at high temperature, and easily regenerated by heating or depressurizing. But, chemically, the reactivity of CaO is weak, friable and become less reactive due to sintering at high temperature.

The activity of a catalyst is determined only by a small fraction of its active sites. This makes the catalyst vulnerable to the presence of small amounts of strongly adsorbed molecules. Strongly adsorbed molecules interact with the active sites to form new compound that has different catalyst activity.

2.3   Temperature Programmed Reduction (TPR) Technique

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 takes place. Among the thermoanalytical techniques, temperature-programmed desorption (TPD) and temperature-programmed reduction (TPR) are the most commonly used tools for characterizing heterogeneous catalysts.

TPR was inspired by the TPD technique and proposed in its present form by Robertson in 1975 for catalysts characterization. (Source: Robertson, McNicol, Baas, Kloet and Jenkins, 1975). In TPR the oxidic catalyst precursor is submitted to a programmed temperature rise under a flow of reducing gas mixture and the consumption of the reducing agent is continuously monitored. TPR provides essential information on the reducibility of these oxidic precursors.

Temperature Programmed Reduction (TPR) provides characterization of the catalyst which is able to analyze the number and quantity of the reducible species present in the sample. (Thermo Finnigan, 1998). Besides that, TPR will also determine the quantity of hydrogen being consumed.

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TPR has been applied to study the influence of support materials, preparation and pre-treatment procedures, and the influence of additives on the reduction behavior of a catalytic material. TPR also reveals possible alloy formation in bi-metallic catalysts. TPR provides a fingerprint of the redox properties of a catalyst, which can be compared with reference thermo grams, and it provides the total consumption of the reducing agent, which can be correlated with the change in the valence state of the reducible substance.

The example of H_2-TPR results of the catalysts are given in Figure 2.2, which shows a broad and strong peak of reduction at about $360^{\circ}C$ for (a) Ni/CaO and a strong peak at $360^{\circ}C$ and a weak peak at $510^{\circ}C$ for (b) Ni/CeO$_2$. (Source: Tang and Lin, 1998).
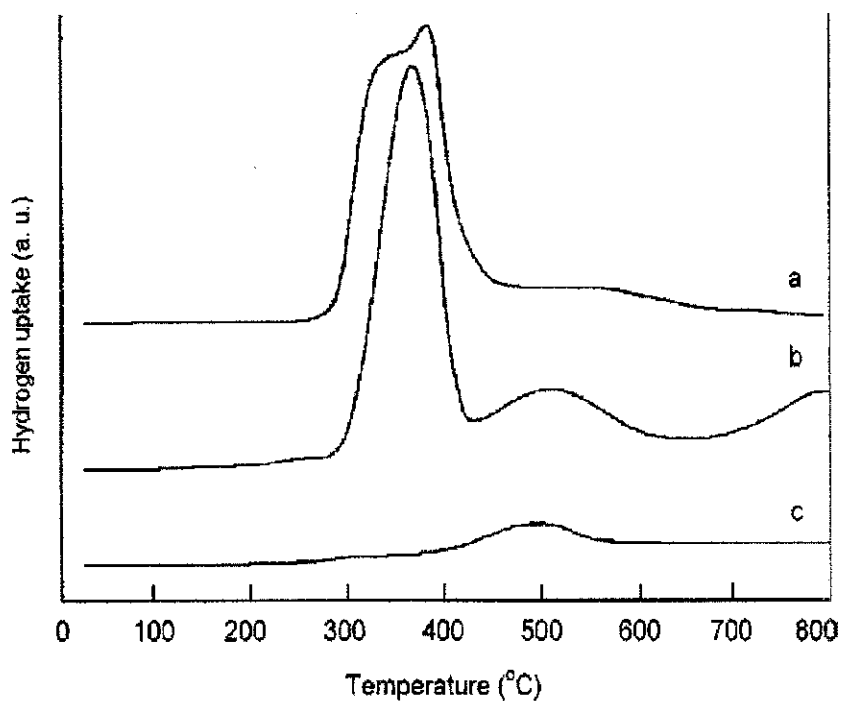
Figure 2.2: TPR profiles of catalyst for a) Ni/CaO b) Ni/CeO$_2$ c) Ni/MgO.

2.4 Temperature Programmed Oxidation (TPO) Technique

Temperature Programmed Oxidation (TPO) determines the temperature range in which sample undergoes oxidation. The results of fresh and spent catalyst will be compared in order to determine the characterization differences of catalyst using TPDRO equipment.

TPO can be used for

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

The case study on temperature-programmed oxidation was included in the work to assess the suitability of TPO for elucidating the kinetics of coke oxidation. In the regeneration, coke oxidizes to form carbon dioxide, along with carbon monoxide and water.

TPO continues to be an important tool for qualitative characterization of the coke. However, the coke burn-off kinetics maybe limited by the diffusion of oxygen into the catalyst pores. The effective diffusivity of gases in the catalyst customarily decreases with coke deposition. (Source: Larachi, F., Belkacemi, K., Hamoudi, S. Sayari, May 2003). Kinetics of carbon evolution in temperature-programmed oxidation of carbonaceous lay down deposited on wet oxidation catalysts.

TPO peak area is proportional to the amount of coke on the catalyst. The amount of contaminant coke correlates with contaminant-metal concentration. The sum of the conversion coke and the graphitic coke correlates with catalyst activity. The high temperature peak assigned to graphitic coke in TPO because graphitic coke is more reactive with oxygen and occurs at higher temperatures.

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The location and nature of coke on spent catalyst affect the coke-oxidation kinetics, which are important factors in catalyst regeneration (Source: Dimitriadis, Lappas, Vasalos, 1998). TPO is a very important tool for characterizing spent catalysts. It can determine the total amount of coke, the hydrogen-to-carbon ratio in the coke, and the location of coke deposited on the spent catalyst.

Figures 2.3 below shows an example of TPO profiles of the deposited carbon over (a) Ni/MgO, (b) Ni/CeO$_2$ and (c) Ni/CaO from pure CH$_4$ and pure CO. As described in the experimental section, they were 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. In addition to the smaller quantity, it also reveals that the oxidative temperature of carbon deposited on Ni/MgO is lower than those of carbon deposited on Ni/CeO$_2$ and Ni/CaO. (Source: Tang and Lin, 1998).
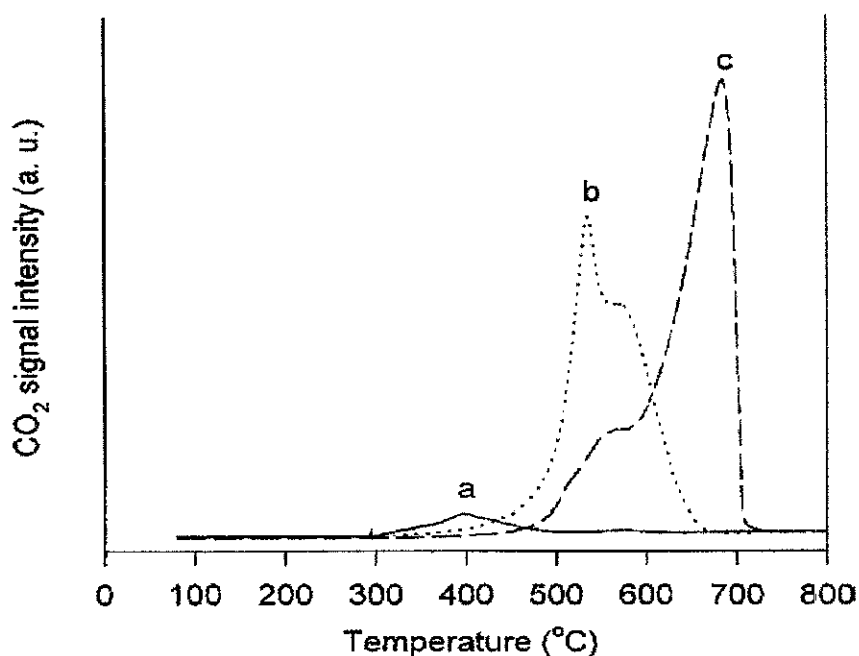
Figure 2.3: TPO profiles of carbon deposited from CO disproportion over a) Ni/MgO b) Ni/CeO$_2$ c) Ni/CaO

2.5   CHNS Technique

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

2.6   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 transitions between the discrete vibrational energy levels of a molecule.

FTIR is used during this research project to identify the functional group of coke and compare the spectra functional group between fresh and spent samples. It depends on the number of waveband. The absorption bands specified in this research project was in the range of $1000 - 4000$ cm^{-1} due to functional group such as $-OH$, $C=O$, and $-CH$. These peaks are characterized by the specific bonds in order to identify the functional group of samples. For example, $-OH$ stretching is at 3500 cm^{-1}, $-OH$ bending is at 1600 cm^{-1} and $-CH$ is at around 2700 cm^{-1} to 3000 cm^{-1}.

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2.7 Coke and regeneration method to improve the catalyst deactivation

The main advantages of the steam reforming process are it could extract the hydrogen not only from hydrocarbon but also from the 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.

The main deactivation of syngas catalyst is coke deposition. Coke can be defined as deposit on the catalyst composed of a mixture of carbon, hydrocarbon, and varying amounts of inorganic compound There are two types of coke typically separated for quantitative analysis, which are soft and hard coke. Hard coke is the portion of total coke that can not be extracted.

Catalytic coke is the hydrogen deficient coke located primarily within the pore structure and is the product of cracking mechanisms. In the steam reforming of CH_4 to syngas, deactivation of supported metal catalysts by coke formation is a serious problem caused by fouling of the metal surface and blockage of the catalyst pores and voids. In the industrial process, a large amount of steam was added in order to avoid coke formation.

Takashi reported that $Ni/Ca_{1-x}Sr_xTiO3$ catalyst prepared by the citrate method from perovskite precursor showed high resistance to coke generation using air as oxidant. (Source: Hayakawa, Harihara, Anderson, York, Suzuki, Yasuda and Takehira, 1996). The high reactivity of the carbon type whisker allows its gasification by hydrogen, carbon dioxide and steam. The whisker structure will collapse as the time increase and will be converted into carbon which is difficult to remove under reducing condition. However, addition of small percentage of oxygen could burn off the carbon.

During the steam reforming of hydrocarbons on nickel reforming catalyst, three typical kinds of carbon species were identified; pyrolytic carbon, encapsulating carbon, and whisker or filamentous carbon. (Source: Rostrup-Nielsen, 1979; Forzatti and Lietti, 1999; Trimm, 1999; Bartholomew, 2001). Pyrolytic carbon is usually obtained by thermal cracking of hydrocarbons above $600^{\circ}C$ and deposition of carbon precursor. Encapsulating carbon is formed by slow polymerization of unsaturated hydrocarbons below $500^{\circ}C$. Meanwhile the whisker carbon is produced by diffusion of carbon into nickel crystals, detachment of nickel from the support and growth of whiskers with nickel on the top of the catalyst above $450^{\circ}C$.

By burning off the deposited carbon with air or oxygen, the catalyst is regenerated. The regeneration method for deactivated catalyst involves the reduction process where by the NiO is reduced to Ni particles at high temperature. This is then followed by an oxidation process and finally another reduction process in order to get back the small particles same as fresh catalyst's performance.

But the problem is the catalyst may be deactivated by sintering, which can cause surface area loss during the catalyst regeneration. Therefore, it is necessary to control the burn off deposited carbon carefully. The regeneration procedures from various sources are simplified in this Table 2.1:

Table 2.1: Regeneration procedure for nickel based catalyst

Catalyst	Regeneration procedure	Remark
Ni/Al$_2$O$_3$ Ni-Cr/Al$_2$O$_3$ (Source: Nichio, Quincoces, Moral, Gonzalez, 2001)	Methane reforming: 1) Regeneration with oxygen flow of 1% O$_2$ in N$_2$ for 2 hour at 1073K. 2) Regeneration with H$_2$ of feed N$_2$/H$_2$ = 9/1 at 923K.	The activity decrease in catalysts regenerated by H$_2$ may be attributed to the permanency deactivating carbon forms and not to the active phase sintering while the regeneration in O$_2$ removes completely the carbon forms but it allows sintering.
Ni/yttria-doped (Source: Jenshi, Yen-Shiun, Ta-Jen, 2004)	CO$_2$ reforming at 500°C under atmospheric pressure: • Regeneration of H$_2$ pre-reduction of catalyst • The gas feed pass through an O$_2$ to eliminate amount of O$_2$. • The catalyst bed purge with flowing argon at 100ml/min for 30 min to remove impurities from catalyst surface. • Afterwards, a feed of CO$_2$: Ar = 25:75 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$_2$O$_3$ (Source: Dias and Assaf, 2004)	Steam reforming; Pass air over the catalyst at high temperature to burn off deposited carbon.	Addition of air to the steam reforming feed results in a decrease in the amount of carbon formed on the catalyst.
Ni-USY (Source: Pawelec, Daza, Fierro, Anderson, 1996)	Benzene hydrogenation: 1) Regeneration in H$_2$ at 673K 2) Firstly with air at 673K for 1 hour and followed by the reduction in H$_2$ for 1hour 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 Chemicals.

Catalysts provided from Industry Company:

1. NiO/CaO Fresh catalyst
2. NiO/CaO Spent catalyst

3.2 Catalysts characterization.

3.2.1. Experimental Procedure for TPR and TPO.

The TPR analysis was carried out under atmospheric pressure, in a continuous flow of hydrogen in the Thermo Finningan equipment, TPD/R/O 1100, which is located at Petrochemical's laboratory. Two samples were analyzed, the fresh and spent catalyst of NiO/CaO. The samples were reduced in a flow of H_2 Temperature-programmed reduction (TPR) of the catalysts was performed by heating the samples from room temperature to 1000^oC at a rate of 20ml/min, in a 10% H_2/Nitrogen gas flow. A weight of 0.02 g catalyst was placed on a quartz wool bed in an external quartz tube, positioned vertically in the oven. The sample was pretreated in order to remove the moisture content before the TPR analysis. The hydrogen consumption for the reduction process was measured by using a thermal conductivity detector (TCD).

The TPO analysis was carried out under atmospheric pressure, in a continuous flow of oxygen in the Thermo Finingan equipment. Two samples were analyzed, the fresh and spent catalyst of NiO/CaO. The samples were oxidized in a flow of O_2 Temperature-programmed oxidation (TPO) of the catalysts was performed by heating the samples from room temperature to 1000^oC at rate of 20ml/min, in a 10% O_2/He gas flow. A weight of 0.02 g catalyst was placed on a quartz wool bed in an external quartz tube, positioned vertically in the oven. The sample was pretreated in order to remove the moisture content

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before the TPO analysis. The oxygen consumption for the oxidation process was measured by using a thermal conductivity detector (TCD).

Sample

Fresh or Spent catalysts' in powder form

Pretreatment

N_2 : 20 ml/min

Ramping factor : 10 ^{O}C/min

Initial temperature : 25 ^{O}C

Final temperature : 110 ^{O}C

TPR

5% H_2 in N_2 : 20 ml/min

Ramping factor : 10 ^{O}C/min

Initial temperature : 25 ^{O}C

Final temperature : 1000°C

TPO

5% O_2 in He : 20 ml/min

Ramping factor : 10 ^{O}C/min

Initial temperature : 25 ^{O}C

Final temperature : 1000 ^{O}C
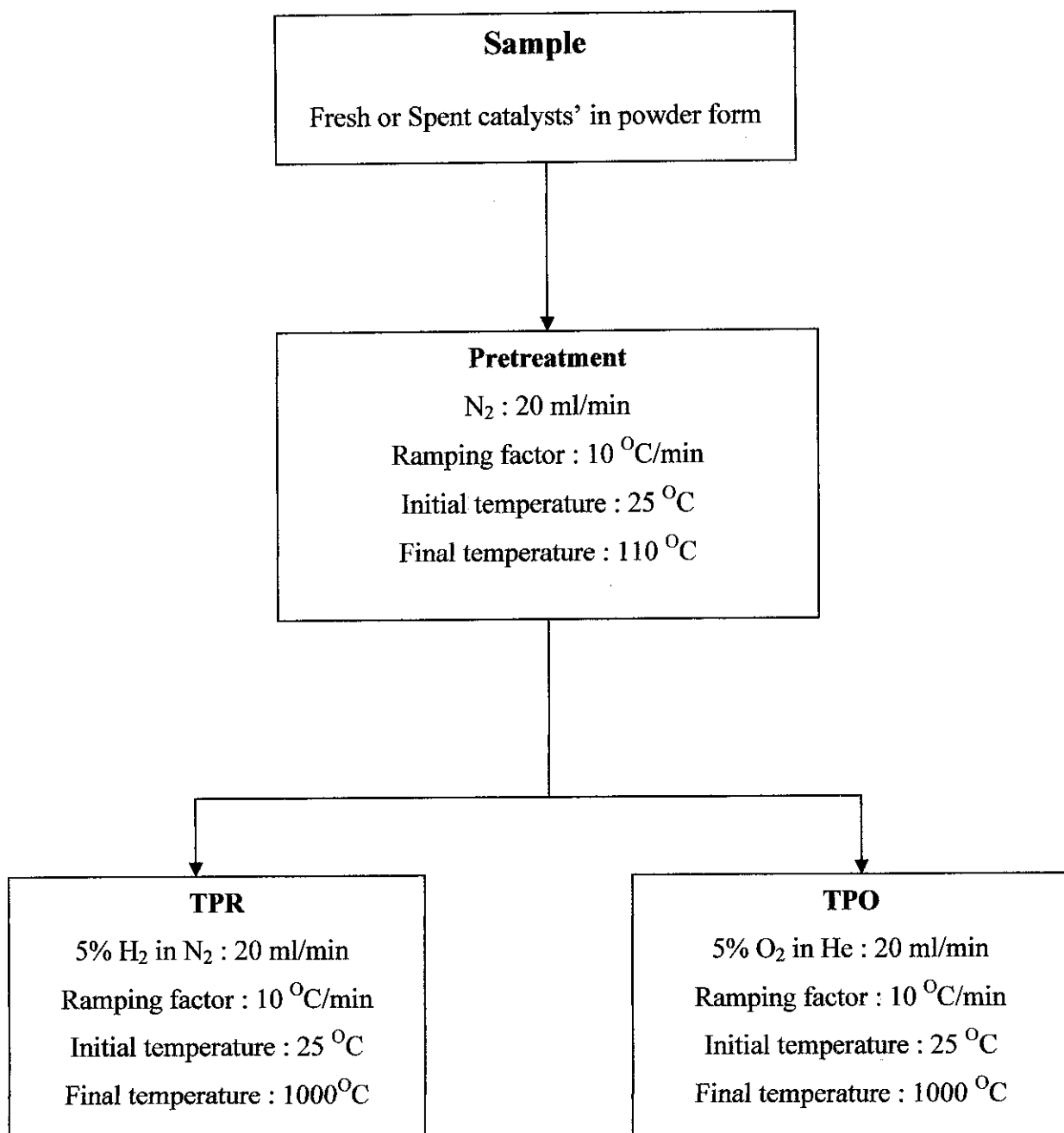
Figure 3.1: Flow diagram for TPR and TPO

3.2.2 Experimental Procedure for CHNS.

```
┌─────────────────────────────────────────────────┐
│                    Sample                        │
│                                                  │
│      Fresh or Spent catalysts' in powder form    │
└─────────────────────────────────────────────────┘
                         │
                         ▼
┌─────────────────────────────────────────────────┐
│               CHNS identification                │
│                                                  │
│  CHNS 932 equipment                              │
│                                                  │
│  -    Sample encapsulated in a tin or silver     │
│  capsule                                         │
│  - The sample is then dropped into the furnace   │
│  at the same time the oxygen passes over.        │
│  -    As the sample enters the combustion        │
│  chamber, oxygen was injected, therefore         │
│  complete oxidation occurred.                    │
│                                                  │
│                                                  │
└─────────────────────────────────────────────────┘
                         │
                         ▼
┌─────────────────────────────────────────────────┐
│                  Analysis and                    │
│                  Discussion                      │
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Figure 3.2 Flow diagram for CHNS

3.2.3. Fourier Transform Infrared Spectroscopy (FTIR)

Fresh and spent catalyst was analyzed using FTIR. It is used to examine the spectra for functional group of catalyst. The samples to be anal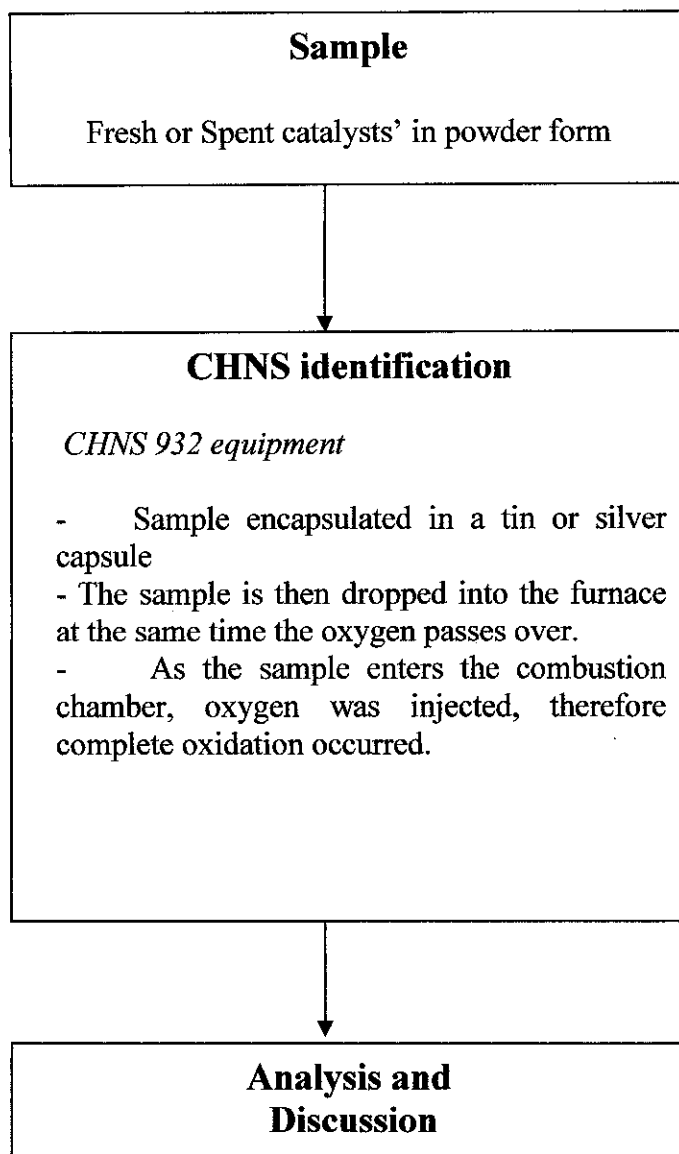yzed were prepared in powder form and dry form to give more curves with sharp peaks. The samples were analyzed using FTIR by following settings:

- Range : start at 4000 cm^{-1} and end at 100 cm^{-1}
- Scan number: 40
- Resolution: 4
- Angle 45°C

Potassium bromide (KBr) was used to improve the scanning effect of catalyst.

The steps of KBr pellet preparation are as below

1. Mortar, pestle pellet holder, 2 bolts and KBr were prepared.
2. Three spatula loads of KBr were measured. This should be 100mg-200mg.
3. One spatula tip of sample was placed in the mortar.
4. KBr was grinded to a very fine powder. This has to be done quickly because the KBr will absorb water from the atmosphere and this makes it difficult to press a good pellet.
5. One bolt was screwed into the pellet holder. About 30-50 mg of the mixture was grounded into cavity and the second bolt was screwed in.
6. The sample should be translucent and it need not be perfectly clear.
7. It was mounted in the spectrometer and make sure that the laser passes through the pellet.
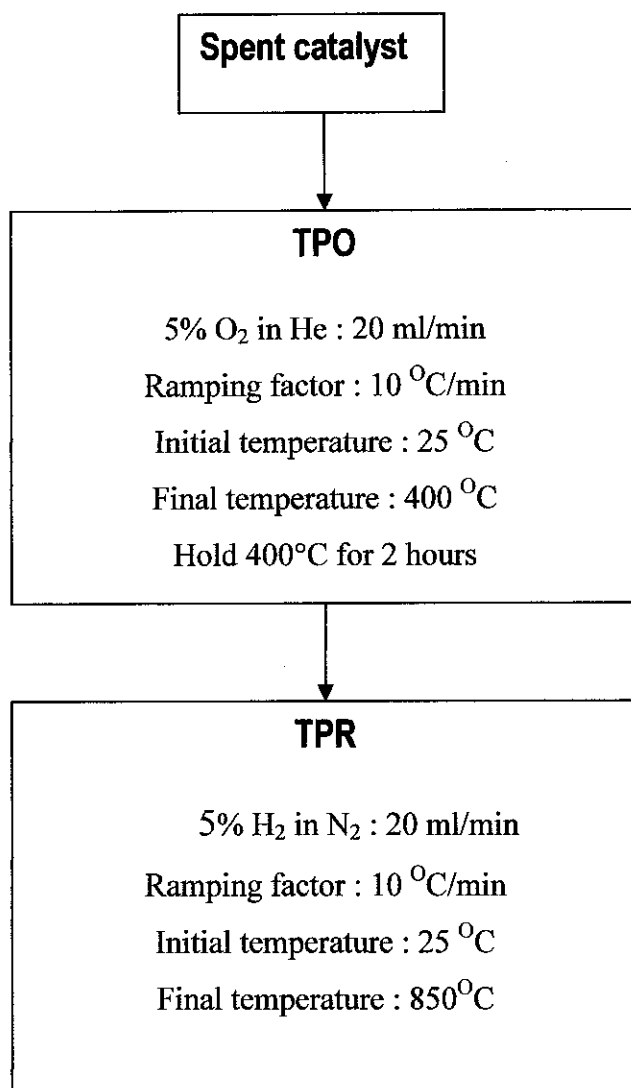
3.3 Regeneration procedure in oxygen atmosphere.

```
┌─────────────────────────┐
│      Spent catalyst     │
└─────────────────────────┘
             │
             ▼
┌─────────────────────────────────────────┐
│                   TPO                    │
│                                          │
│        5% O₂ in He : 20 ml/min           │
│        Ramping factor : 10 °C/min        │
│        Initial temperature : 25 °C       │
│        Final temperature : 400 °C        │
│        Hold 400°C for 2 hours            │
└─────────────────────────────────────────┘
             │
             ▼
┌─────────────────────────────────────────┐
│                   TPR                    │
│                                          │
│        5% H₂ in N₂ : 20 ml/min           │
│        Ramping factor : 10 °C/min        │
│        Initial temperature : 25 °C       │
│        Final temperature : 850°C         │
└─────────────────────────────────────────┘
```

TPO

5% O_2 in He : 20 ml/min

Ramping factor : 10 $^{\circ}$C/min

Initial temperature : 25 $^{\circ}$C

Final temperature : 400 $^{\circ}$C

Hold 400°C for 2 hours

TPR

5% H_2 in N_2 : 20 ml/min

Ramping factor : 10 $^{\circ}$C/min

Initial temperature : 25 $^{\circ}$C

Final temperature : 850°C

Figure 3.3: Flow diagram for regeneration procedure

3.4 Equipment required

TPDRO, CHNS, FTIR

CHAPTER 4

RESULTS AND DISCUSSION

4.1 TPR analysis

Table 4.1 : Observation of the catalyst before and after TPR analysis

Sample	Before Analysis	After analysis
Fresh catalyst	Grey	Black powder
Spent catalyst	Grey	Black powder

Table 4.2 : Amount of hydrogen uptake and reduction temperature of catalyst

Sample		Hydrogen uptake ($\mu mol/g$)	Reduction temperature (^{o}C)
Fresh catalyst	First peak	1454.76	410
	Second peak	176.35	680
Spent catalyst	Third peak	303.33	640
	Fourth peak	51.06	900

From the TPR plot shown in Figure 4.1, two peaks were observed for the fresh catalyst, while four peaks were observed for the spent catalyst of NiO/CaO. The presence of addition two peaks for the spent catalyst curve indicates contaminants, such as coke deposition. The orange line is for the fresh catalyst and the red line for the spent catalyst. NiO/CaO catalyst is easily reduced since it shows lower temperature range for the first peak, which is at $410^{o}C$. The second peak temperature for the fresh catalyst is at $680\ ^{o}C$. The spent catalyst demonstrates four peaks, which are at $280^{o}C$, $400\ ^{o}C$, $640^{o}C$, and $900^{o}C$.

In TPR curve, the fresh catalyst reduction starts at 300 °C and the peak maximum temperature is 410 °C. For the spent catalyst reduction starts at 220 °C and the peak maximum temperature is at 640 °C. As the temperature reaches 960 °C, the reduction curve reached back to 0mV signal. From TPR plot, it is observed that there are two particle size distributions. The lower reduction temperature range refers to the reduction process for smaller particles size, while the higher reduction temperature range refers to the reduction nickel particles process for bigger particles.

The area under TPR curve represents the total amount of hydrogen consumption and is commonly expressed in terms of μmoles of H_2 consumed per mol of metal atoms. For fresh catalyst, the hydrogen consumption is very high, which is 1454.76μmol/g of NiO/CaO being reduced at 410°C. For second reduction peak, the amount of hydrogen consumed is 176.35μmol/g. Meanwhile for spent catalyst, the corresponding amounts of hydrogen for the third and fourth reduction peaks are 303.33μmol/g and 51.06μmol/g, respectively. This indicates that more nickel oxide particles, since more hydrogen consumed to reduce the NiO to Ni°. On the other hand, the total amount of hydrogen used for reduction is 1631.11μmol/g for fresh and 354.39μmol/g for spent catalyst. This indicates that there is nickel particles loss during reaction since the total amount of hydrogen consumed μmol/g is less for the spent catalyst.

Temperature at which the reduction itself takes place can be observed from the positive peak in the graph. For spent catalyst, the first peak indicates the existence of hydrated water and this is supported from the FTIR spectra of the samples. The second peak corresponds to the reduction of NiO by consumption amount of hydrogen from the stochiometry equation.

$$NiO + H_2 \rightarrow Ni^{\circ} + H_2O$$
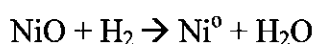
The third and fourth peak for spent catalyst, which is at 600°C and 900°C; consistent with the literature reported by Santos et al., 2004. The fourth peak for spent catalyst corresponds to the presence of calcium carbonate, which is supported by results from FTIR, where carbonate exists in the spent sample. It is observed that the hydrogen consumption for fresh catalyst is higher compared to the spent catalyst at low temperature. This indicates that there are more NiO particles in the fresh catalyst.

From the TPR plot, it is observed that the nickel species for spent catalyst has been sintered. This is because of the catalyst initially from small particles become big particles due to the sintering at high temperature. The aggregation of nickel particles dominated the activity change due to large metallic particles generated during the reduction process. (Source: Qiangshan Jing, Hui Lou, Liuye Mo, Jinhua Fei and Xiaoming Zheng, p.297). After the NiO/CaO catalyst was reduced in a flow of H_2 at 700°C for 1 hour, the peak of NiO disappeared and was replaced by metallic nickel, indicating the complete reduction of NiO to Ni. (Source: Tang and Lin, 1998).

It is well known that at low temperature, the spent catalyst has small Ni particles. Carbon does not deposit easily in small particles since the formation of carbon filaments require a great amount of near active sites, in order to initiate carbon polymerization. With smaller particles, the possibility of polymerization decreases, which eases the gasification of the carbon that its polymerization. (Source: Dias and Assaf, 2004). This means that in small particles, more nickel active sites are available for reactants because of high surface area and less carbon deposition. Therefore, it needs low temperature to remove the carbon deposit since the carbon does not easily deposit in small nickel particles.

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4.2 TPO analysis

Table 4.3 : Observation of the catalyst before and after TPO analysis

Sample	Before Analysis	After analysis
Fresh catalyst	Grey	Green powder
Spent catalyst	Grey	Green powder

Table 4.4 : Amount of oxygen uptake and oxidation temperature of catalyst

Sample		Hydrogen uptake (μmol/g)	Reduction temperature (^{o}C)
Fresh catalyst	First peak	18.12	440
Spent catalyst	First peak	106.19	460
	Second peak	77.61	800

From the TPO plot shown in Figure 4.2, one peak was observed for the fresh catalyst, while two peaks were observed for the spent catalyst of NiO/CaO. The presence of addition two peaks for the spent catalyst curve indicates the contaminants, such as coke deposition.

From the findings based on some literatures, it is observed for the spent catalyst, the lower oxidation temperature range indicates the oxidation process for nickel particles, while the higher oxidation temperature range is attributed to the presence of carbonate species for the spent catalyst. This is supported by the FTIR spectra of the samples.

The blue line is the fresh catalyst and the red line is the spent catalyst. The fresh catalyst is easily oxidized since it shows lower temperature range for the first peak, which is at 440°C. The spent catalyst demonstrates two peaks, which are at 460°C, and 800°C. TPO profiles of carbon deposits on various Ni catalysts after 2 hours coking are

illustrated in this literature, Shaobin Wang and GQ Lu, 2000. It is observed that the oxidation of carbonaceous species on nickel species starts at 450°C.

In the TPO curve, the fresh catalyst oxidation starts at 200°C and the peak maximum temperature is at 440°C. For the spent catalyst, oxidation starts also at 220°C and the peak maximum temperature is at 800°C. As the temperature reaches 940°C and stabilizes, the curve reached back to 0mV signal.

The area under TPO curve represents the total amount of oxygen consumed and is commonly expressed in terms of moles of O_2 consumed per mol of metal atoms. For fresh catalyst, at 440°C the oxygen consumption is 18.12μmol/g, which is less compared to the spent and this result is consistent with TPR plot. This indicates there is more nickel oxide in the fresh catalyst and this result is consistent with TPR plot. For spent catalyst, the amount of oxygen consumed is high compared to other peaks, which is 106.19μmol/g to oxidize NiO/CaO. The corresponding amount of oxygen for the second peak is 77.61μmol/g.

Temperature at which the oxidation itself takes place could be observed from the positive peak in the graph. The first and second peak corresponds to the oxidation of Ni metal by additional amount of oxygen and coke at 460°C and 800°C. The TPO profiles of the carbon deposition from CH_4 decomposition over Ni/CaO are at 490°C and 720°C. (Source: Tang and Lin, 1998). There is high content of carbonate ($CaCO_3$) and no coke present in the spent catalyst, which is supported by the results from FTIR analysis. The FTIR spectrum shows only –OH and CO_3^- functional group without any hydrocarbon content.

The ageing of deposited carbon over Ni/CaO may be slow down due to some extent. (Source: Tang and Lin, 1999). The nature of the coke formed was studied by the TPO experiments. After NiO/CaO catalyst is oxidized in a flow of O_2 in Helium at 1000°C for 2 hours, the peak of NiO in spent catalyst was shifted towards high

temperature, indicating that the spent catalyst is affected by other contaminants or impurities.

The difference of the oxidation temperature indicates that the carbon type was formed on the catalyst surface. The carbonate at 800°C is difficult to oxidize since the catalyst might be the carbon that has a long-range order, which can be classified as pyrolitic carbon. Pyrolytic carbon is usually obtained by thermal cracking of hydrocarbons above 600°C and deposition of carbon precursor. (Source: Rostrup-Nielsen, 1979; Forzatti and Lietti, 1999; Trimm, 1999; Bartholomew, 2001).

TPO of deposited carbon shows that the catalyst consumed a significant amount of oxygen, which only a fraction reacts with surface carbon species, indicating that surface oxygen plays a significant role in controlling the carbon formation. Several groups have also reported an influence of Ni particle size on the coke formation rate during methane to syngas reactions, resulting in an increased selectivity to coke formation at increasing Ni particle size.

In the case of CaO-promoted catalyst, CH_4 decomposition seems to dominate the coking process. (Source: Shaobin Wang and GQ Lu, 2000). The coke formation and Ni sintering cause the simultaneous decrease in activity towards syngas formation. It indicates that the Ni particles reach its critical size when the coke formation dominates, thus leading to coverage of such Ni particles by carbon. (Source: Lercher et al., 1996).

4.3 Regeneration analysis

4.3.1 Regeneration in oxygen atmosphere at 400°C

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, the oxidation process at 400°C for two hours had been done first and followed by TPR until 850°C. It is observed that there is one peak, which is at 400°C for the TPO plot shown in Figure 4.3 and three peaks are observed in the TPR plot shown in Figure 4.4.

From TPR plot shown in Figure 4.4, the ratio intensity of signal between the second peak and first peak is 9.4, which indicates there are more big particles of nickel in the regenerated catalyst. Then, the author compared them with the spent sample; it shows that the lower particles range in the 400°C regenerated sample has more intensity than the spent sample intensity. This indicates that there are nickel oxide particle recovered during the treatment since it consumed more hydrogen. Then, the author compared with the original spent sample ratio. The original spent sample is 10.2, meanwhile the regenerated sample at 400°C is 9.4. This means that the ratio is reduced and it is suggested to further reduce the ratio to 0.32 as fresh sample compare with the original TPR for fresh catalyst from Figure 4.1. From TPR plot Figure 4.1, shows that there are more small particles size in lower temperature range.

The purpose of regeneration is to remove coke and improve the catalyst performance. From TPR plot in Figure 4.1, it is clearly observed that the particle is sintered at higher temperature. The purpose of this project is to improve the catalyst performance by regenerating the spent catalyst, remove coke and produce smaller particle which is similar to the fresh catalyst. For lower temperature, the energy consumed and cost is lower compared to higher temperature. Therefore, the author started regeneration at lower temperature, 400°C and it shows that the lower particles range intensity is increased.

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4.3.2 Regeneration in oxygen atmosphere at 600°C

For the second trial regeneration, the author did in the oxygen atmosphere at 600°C for two hours and followed by TPR until 850°C. It is observed that there is one peak, which is at 560°C for the TPO plot shown in Figure 4.5 and three peaks are observed in the TPR plot shown in Figure 4.6.

From the TPR plot, the ratio of peak intensities between the second peak and first peak is 5.5, which indicates that the big and small Ni particles are equally distributed in term of quantity in this regenerated sample at 600°C. This indicates that regeneration at 600 °C manages to redistribute the particle size in the spent catalyst. Compared to the spent sample; the regenerated catalyst displayed higher amount of small Ni particles. This indicates that there is more nickel oxide particles being recovered during the oxidation temperature at 600°C.

For the original spent sample the ratio between the second peak and first peak is 10.2, while the regenerated sample at 600°C is 5.5. This means the ratio is reduced and it is suggested to further reduce the ratio to 0.32 as fresh sample. It is shown clearly in Figure 4.7, the comparison between regenerated sample for spent catalyst at 400°C and 600°C. It is concluded that regeneration in oxygen atmosphere at 600 °C manages to redistribute the particles size in spent catalyst.

4.4 CHNS analysis

Table 4.5 : Percentage amount of carbon and hydrogen in the fresh catalyst

Fresh NiO/CaO		
Reading no.	C (%)	H (%)
1	0.291	-0.097
2	0.251	-0.094
3	0.275	-0.096
average	0.272	-0.096

Table 4.6 : Percentage amount of carbon and hydrogen in the spent catalyst

Spent NiO/CaO		
Reading no.	C (%)	H (%)
1	0.911	-0.096
2	0.840	-0.095
3	0.840	-0.095
average	0.864	-0.095

From the CHNS analysis results above, it shows that an increase in carbon content for the spent catalyst sample, and finally no change in hydrogen content. The increment in carbon content has indicated that the spent catalyst is highly content with carbonate and no coke was found. Most of hydrogen results are below the detectable limit.

4.5 FTIR (Fourier Transform Infrared Spectroscopy Spectrum) analysis

The results of the analysis on fresh and spent catalyst based on FTIR are shown in Figures 4.8 and 4.9. The sample contains some moisture and some broader bands caused by the hydrogen bonding. They may be a characteristic of molecular symmetry, or combination bands arising from multiple binds deforming simultaneously.

Figure 4.8 represents the FTIR spectrum of fresh catalyst. The band observed at 3450 cm^{-1} indicates the existence of –OH stretching, might be from moisture. The band observed at 1635 cm^{-1} is due to -OH bending.

Figure 4.9 represents the FTIR spectrum of spent catalyst. The band observed at 3500 cm^{-1} indicates the existence of –OH stretching. The band observed at 1635 cm^{-1} is due to -OH bending, the bands at 1479 cm^{-1} and 1066 cm^{-1} indicate the existence of CO_3^{-}. There is no indication for the presence of hydrocarbon since there is no adsorption bands are observed at 3500 cm^{-1} to 2800 cm^{-1} wave number.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

For the literature research part, the required information regarding NiO/CaO physical properties such as reduction and oxidation temperatures have been identified. 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 (TPR) analysis, samples' characteristic such as temperature at which the reduction itself takes place and the amount of hydrogen consumed has been observed. From the TPR plot, it is observed that amount of hydrogen in the fresh catalyst is more compared to the spent catalyst. This indicates that there are more NiO particles in fresh to reduce from NiO to Ni^0. For the spent catalyst, two additional peaks compared to the fresh catalyst were observed indicating the presence of contaminants. The species identified at reduction temperature $900^{\circ}C$ is carbonate. For the fresh catalyst, nickel species were reduced at $410\ ^{\circ}C$ and $680\ ^{\circ}C$, while for the spent catalyst, the reduction temperatures for nickel catalyst were reduced at $400^{\circ}C$ and $640^{\circ}C$. It is observed that there were two particle size distributions of nickel species. Lower reduction temperature range which is around $400^{\circ}C$ is for smaller particle size distribution and the higher reduction temperature range which is around $600^{\circ}C$ is for the bigger particle size distribution.

Temperature programmed oxidation (TPO) analysis provides the characterization at which is able to determine the oxidation temperature of species present in the catalyst. From the TPO plot, it is observed that at lower temperature indicates the presence of nickel species, meanwhile at high temperature indicates the presence of carbonates species. This has been approved by literature and other characterization techniques using FTIR and CHNS equipment.

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From FTIR analysis, the functional group of fresh and spent catalyst is identified. The functional group present in fresh sample is –OH and for spent are -OH and carbonate. CHNS is another method to characterize catalyst through determining the catalyst's performance and physical properties. It detects the percentage of carbon, nitrogen, sulfur and hydrogen contents. From the experiment, the CHNS analysis shows that high amount of carbon content from carbonate for spent catalyst.

From both two analysis, TPR and TPO, it is necessary to determine the regeneration method which can improve the catalyst performance similar to the fresh catalyst. For regeneration at 400°C shows that larger particles range has higher amount of intensity compare to smaller particles range, meanwhile for regeneration at 600°C show that equal particles distribution for larger and smaller particles range. It is concluded that regeneration in oxygen atmosphere at 600 °C manages to redistribute the particles size in spent catalyst.

5.2 Suggested future work for continuation project

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

1. Other characterization technique such as AAS (Atomic Absorption spectrometry) have to be used in order to determine the nickel composition present in the catalyst.

2. For TPR and TPO experiments, it is recommended to connect with mass spec to determine the species present accurate, precisely and immediately.

3. For regeneration part, increase the oxidation temperature to 700°C or 800°C to observe the TPR result and compared with the fresh TPR plot.

4. During the regeneration analysis, it is recommended to carry out he regeneration in hydrogen instead of oxygen.

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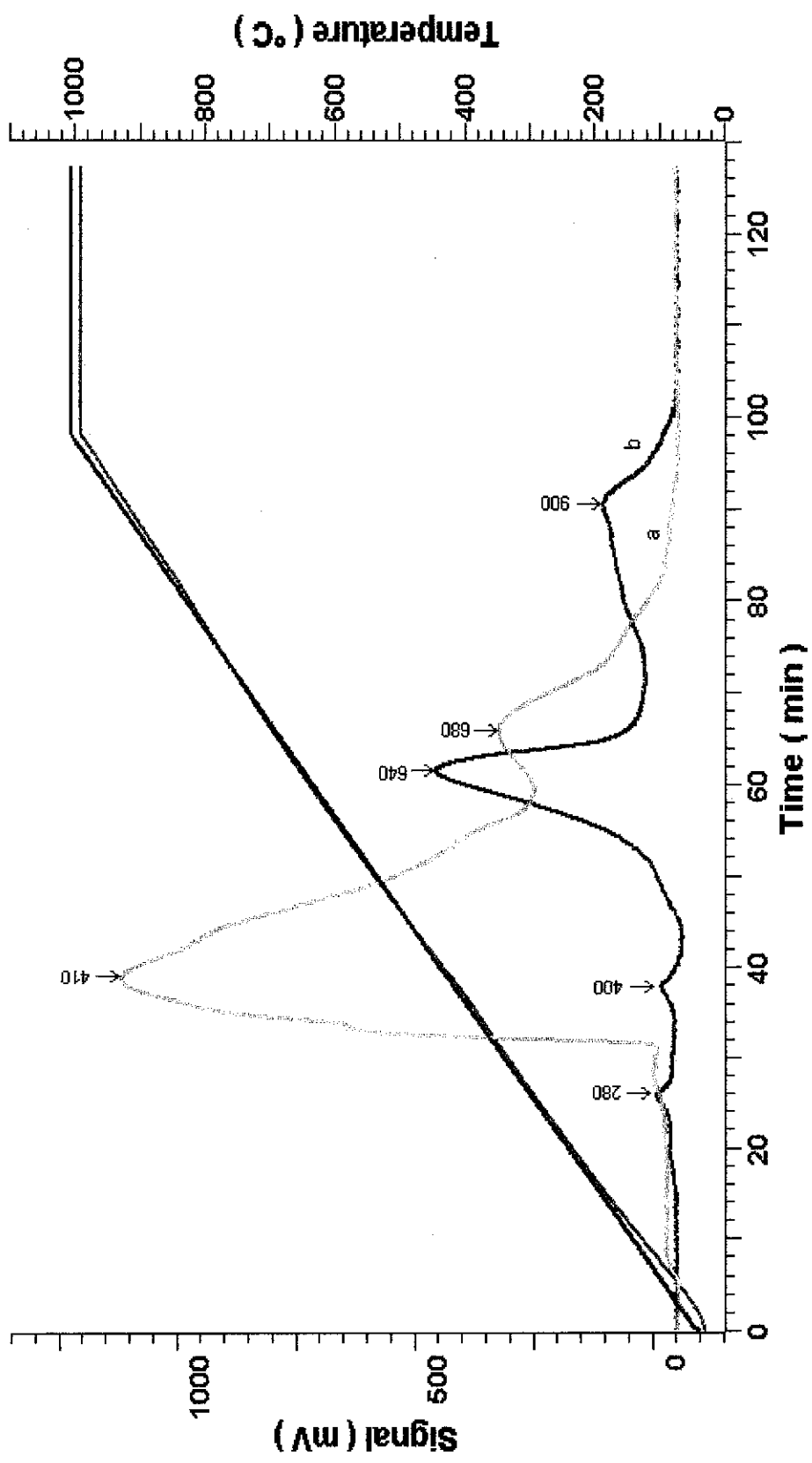
22. www.scej.org/ronbun/JCEJe/e27p0727.html

Figure 4.1 : TPR profiles for NiO/CaO catalyst a) Fresh sample b)Spent sample
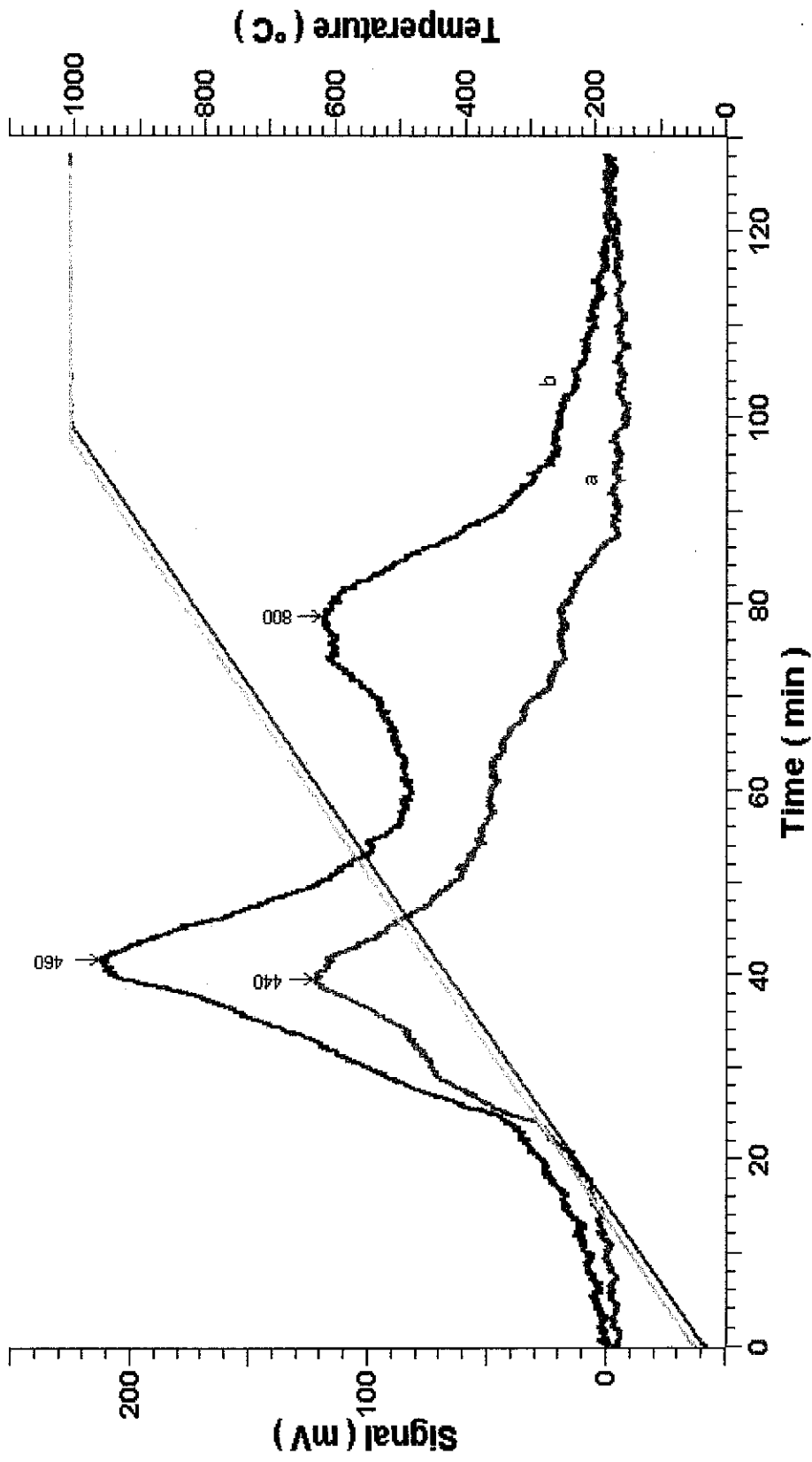
Figure 4.2 : TPO profiles for NiO/CaO catalyst a) Fresh sample b)Spent sample
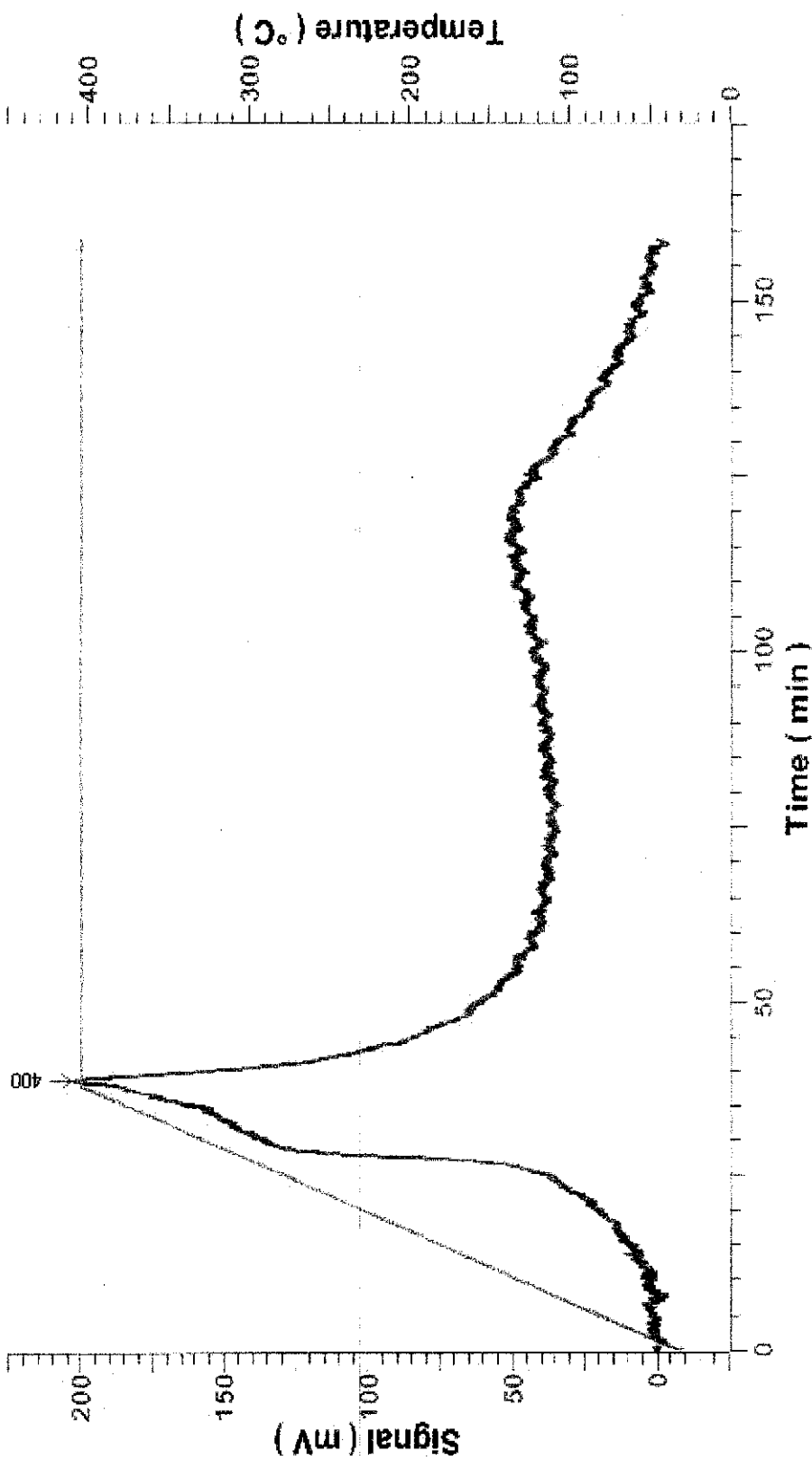
Figure 4.3 : TPO profiles for spent catalyst after regenerated at 400°C
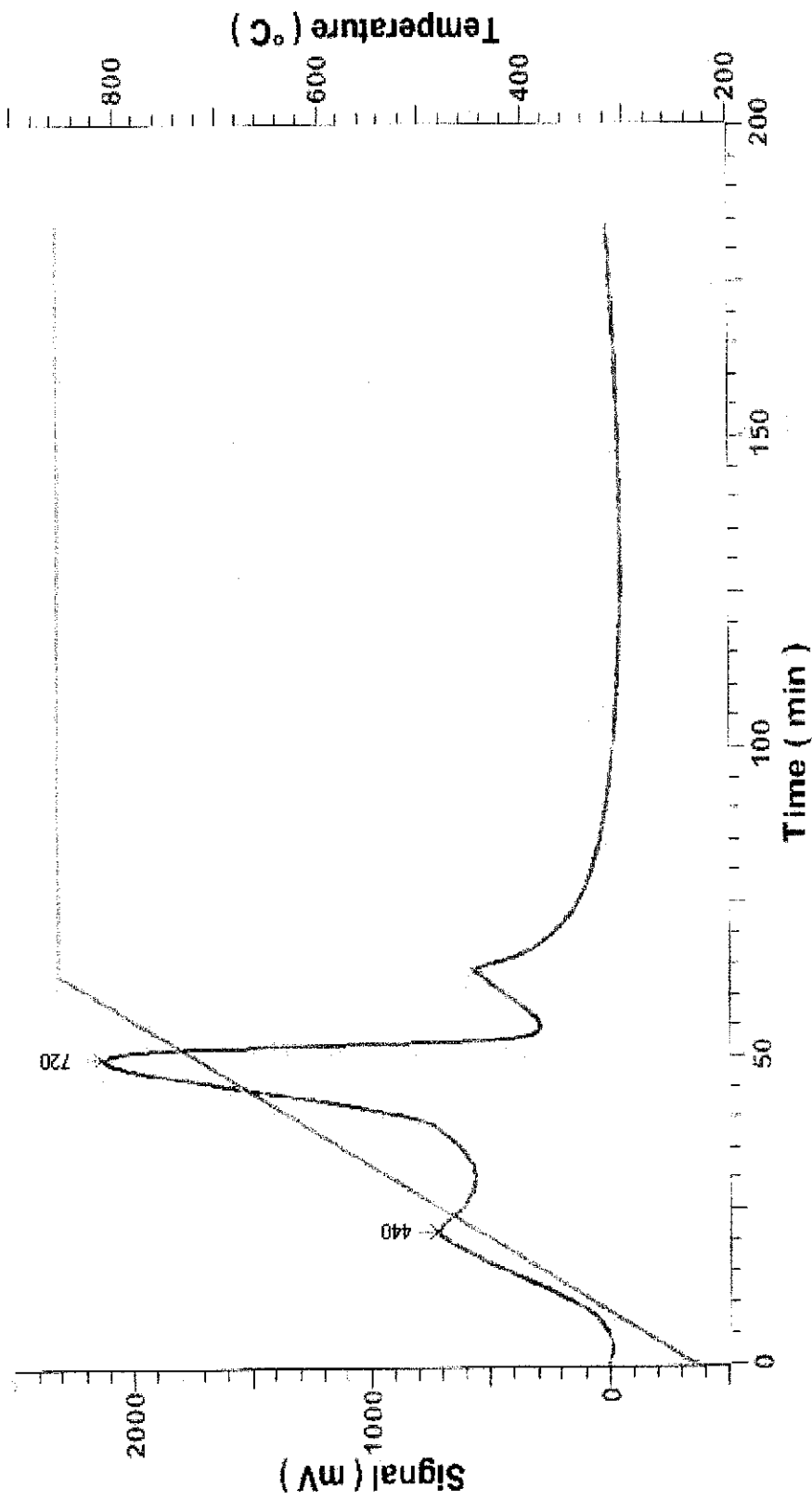
Figure 4.4 : TPR profiles for spent catalyst after regenerated at 400°C
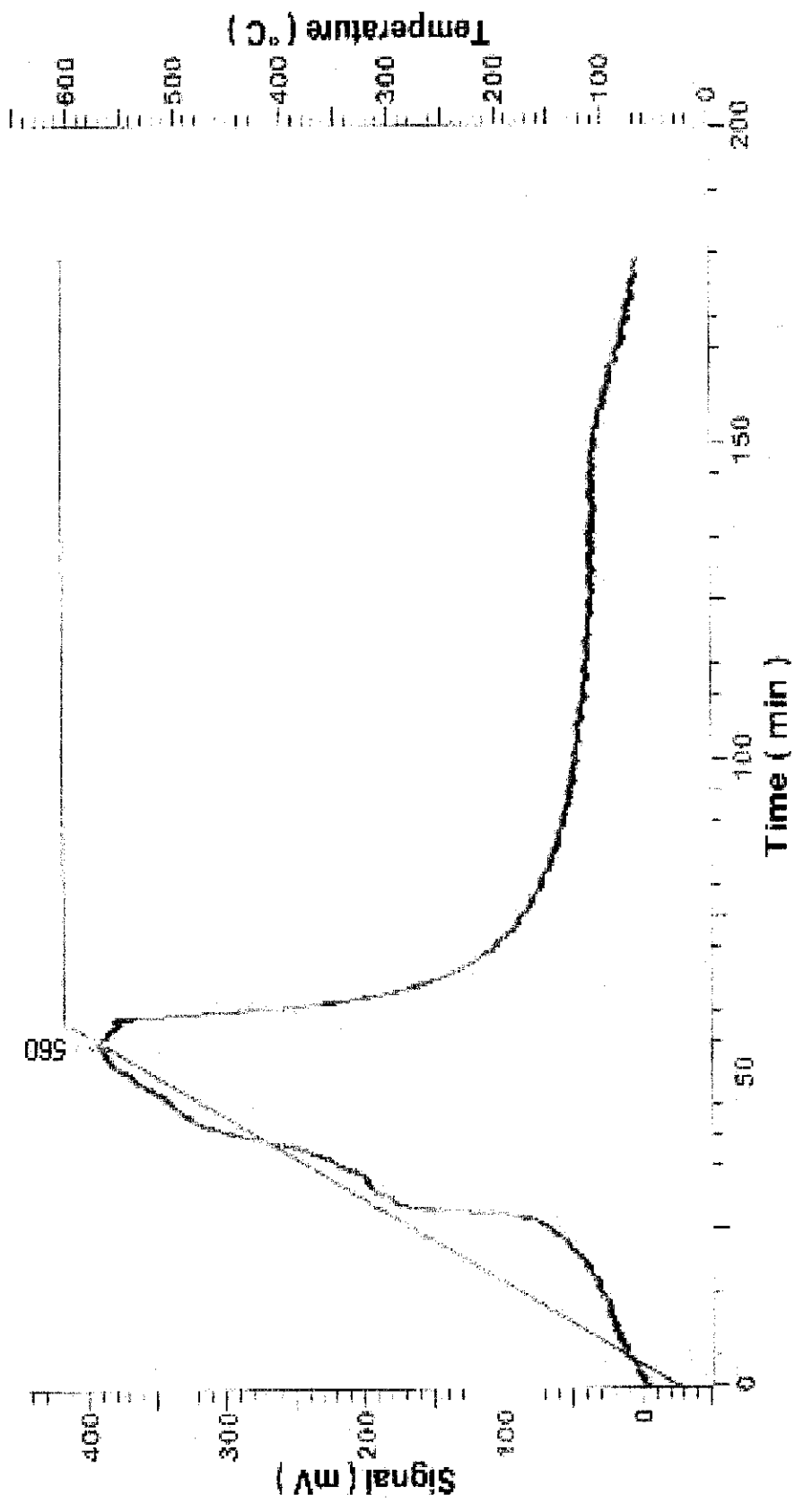
Figure 4.5 : TPO profiles for spent catalyst after regenerated at 600°C
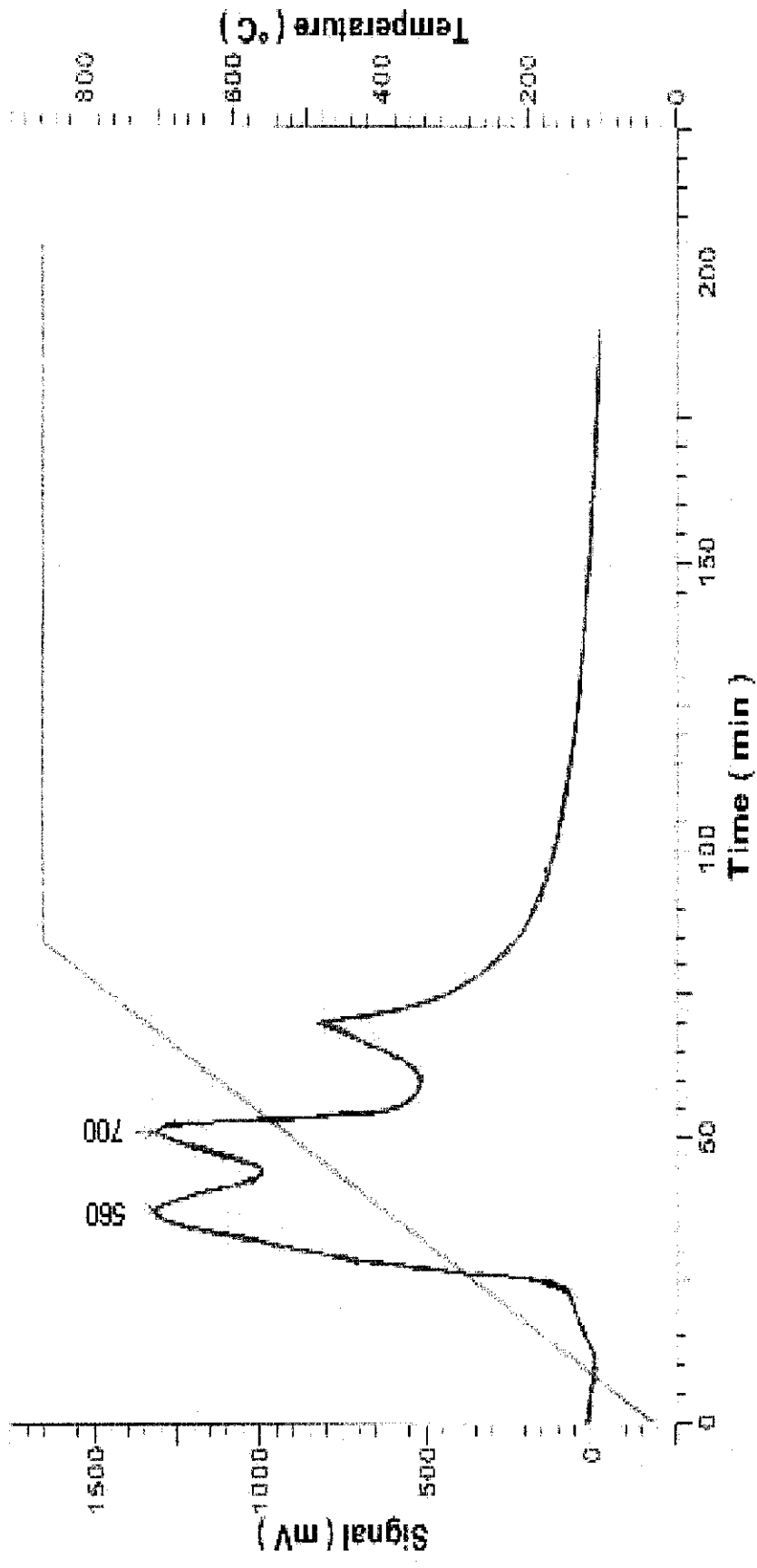
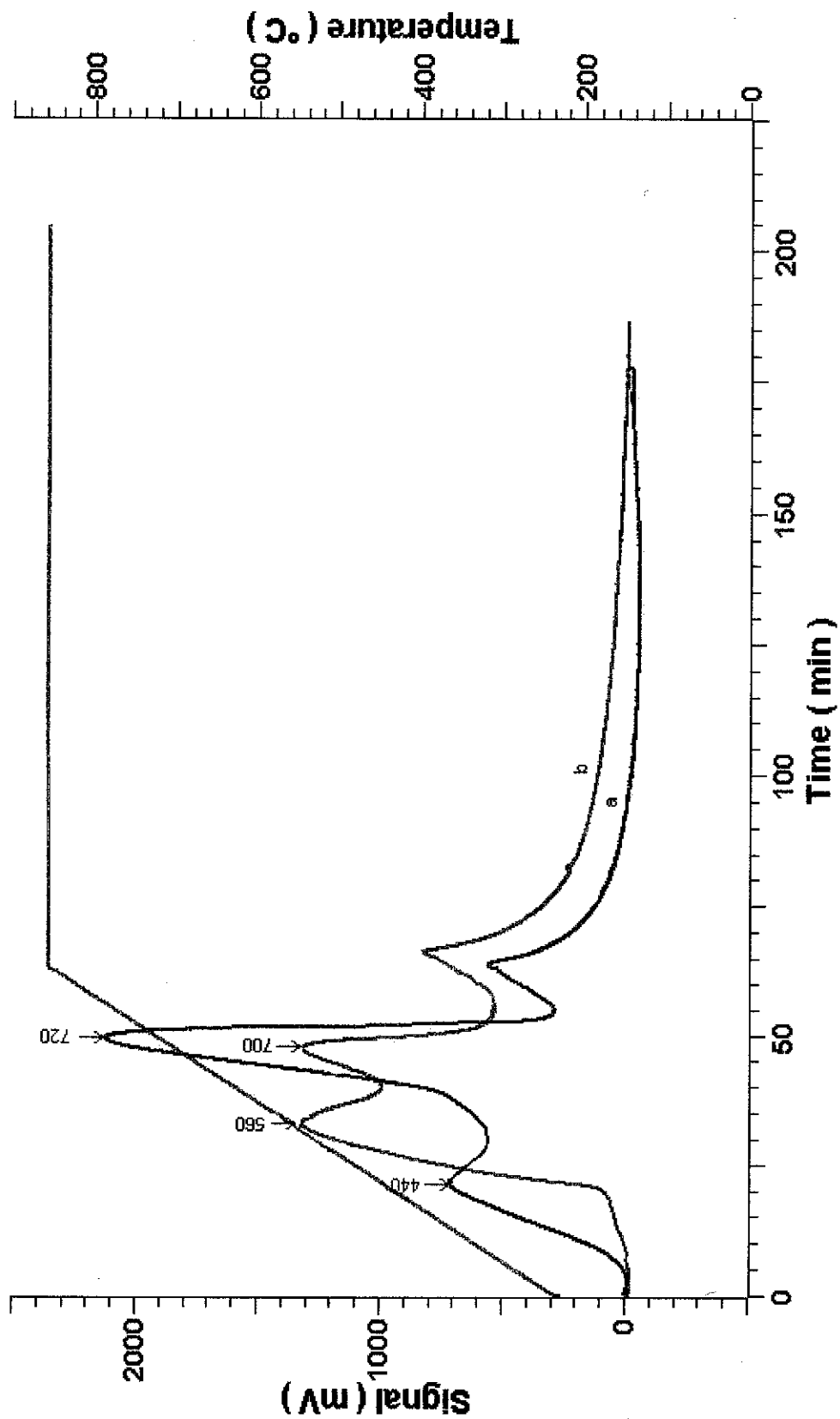Figure 4.6 : TPR profiles for spent catalyst after regenerated at 600°C

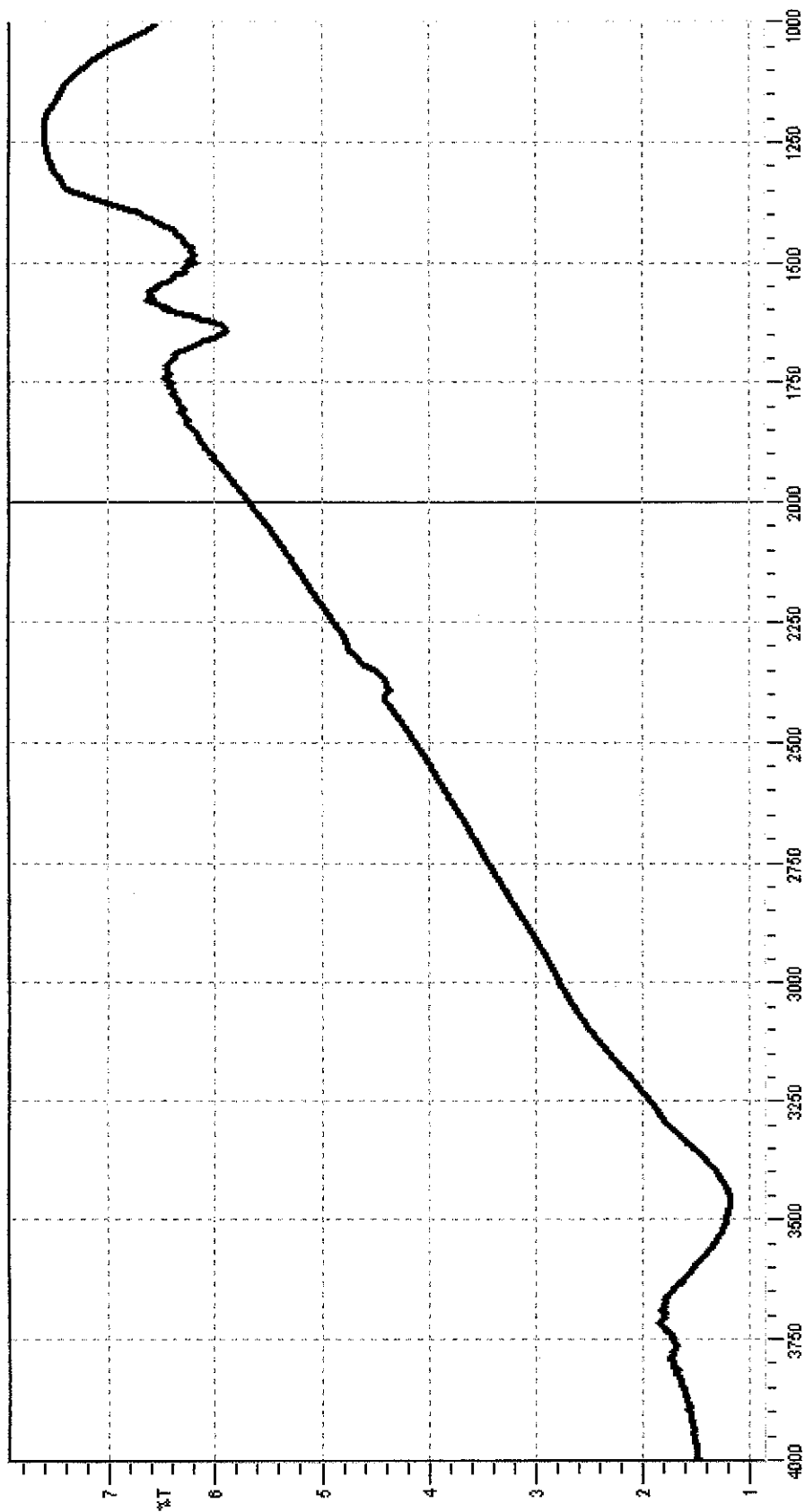Figure 4.7 : TPR profile for spent catalyst after regenerated a) oxidation temp at 400°C b) oxidation temp at 600°C
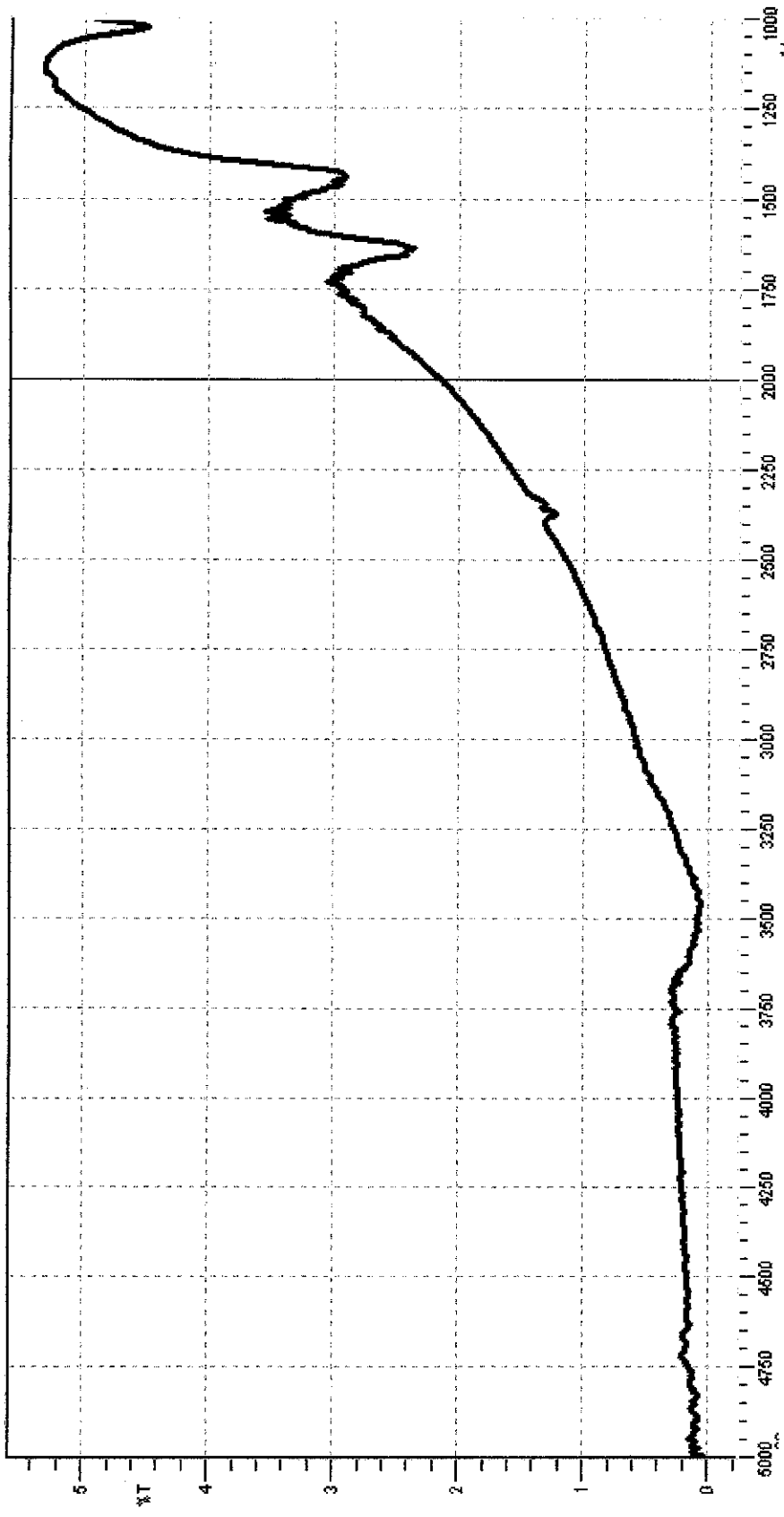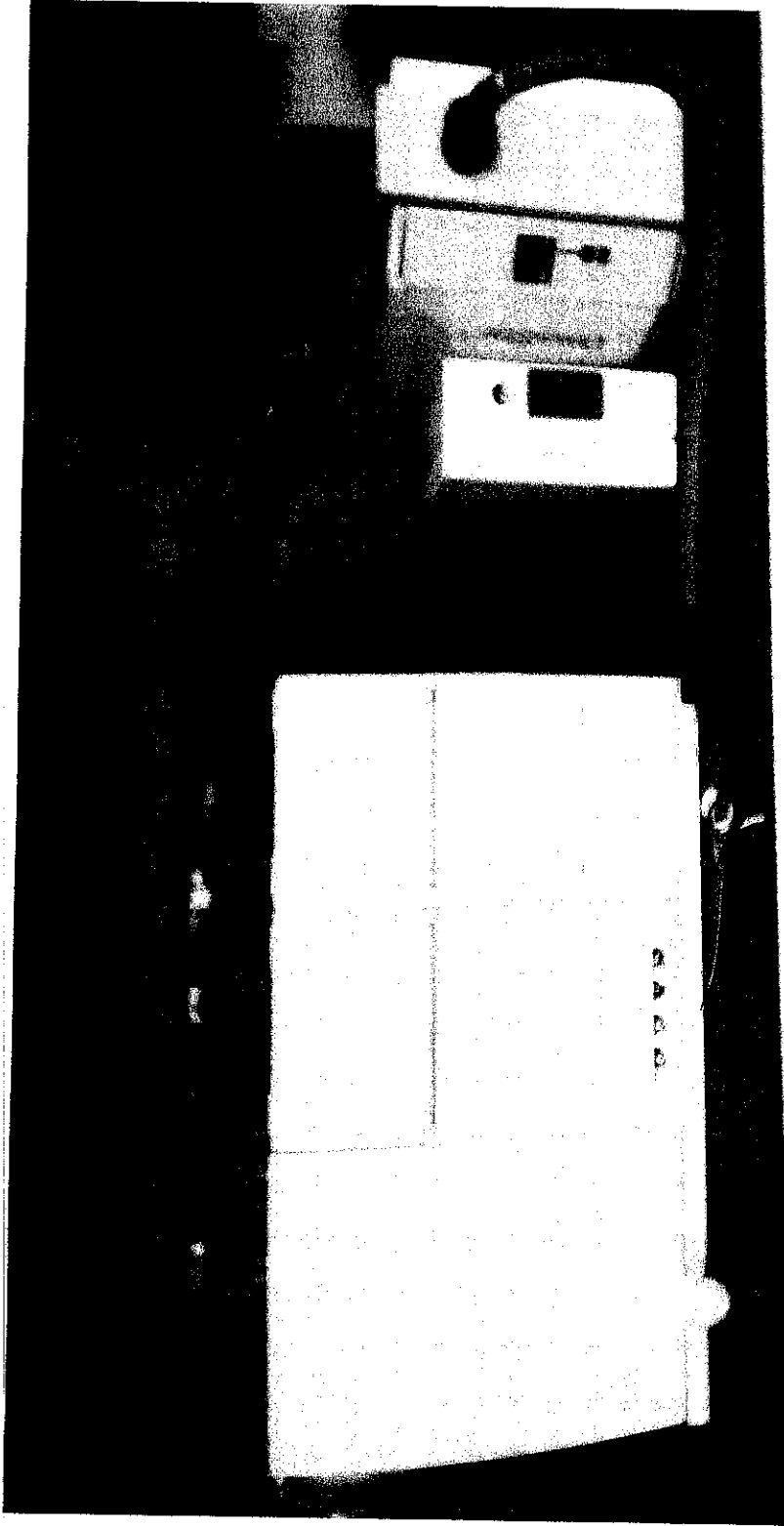
Figure 4.8 : FTIR plot of fresh catalyst

Figure 4.9 : FTIR plot of spent catalyst

Appendix 1　TPDRO equipment from side view