Synthesis Gas Production via CO_2 Reforming Using Ni-Based Catalysts

by

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15188

Dissertation submitted in partial fulfilment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

MAY 2014

CERTIFICATION OF APPROVAL

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A project dissertation submitted to the

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Approved by,

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(Dr. Bawadi Abdullah)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

MALAYSIA

May 2014

CERTIFICATE 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.

(ROSE DIYANAH BINTI ROSDIN)

ABSTRACT

This project has a main objective namely the development of nickel, Ni-based catalyst for the synthesis gas (syngas) production via CO_2 reforming of methane. The production of syngas via dry reforming has not been commercialized due to unavailability of a suitable catalyst which is active and have low deactivation rate. The main issue on the dry reforming catalyst is the coke deposition and sintering of catalyst particles. Therefore, this project will focus on development of coke-free and highly dispersed Ni-based catalyst for the CO_2 reforming reaction.

The project aims to develop Ni-based catalyst for CO_2 reforming process by synthesizing via impregnation method on various oxide supports. The Ni-based catalysts will be characterized in terms of particle size, surface area, porosity, phase, surface composition and reducibility properties. The characterization will be done by various microscopic and spectroscopic methods. Then, the activity of the Ni-based catalyst in the CO_2 reforming will be studied in a high-temperature fixed bed micro-reactivity reactor. The dependence of the products composition (H_2:CO ratio) on the catalyst properties will be monitored

This work studied the performance of Ni-based catalysts supported with various oxides supports (ZrO_2/Al_2O_3, MgO/Al_2O_3) for the production of synthesis gas through CO2 reforming of CH_4. The catalysts were prepared by impregnation method. The catalysts were characterized by BET, XRD, FESEM, TEM and EDX analysis. According to XRD, good interaction between active phase and support can be observed in Ni/MgO-Al_2O_3 catalyst. The morphology in Ni/MgO-Al_2O_3 is uniform, besides having well dispersed particles on active sites. The Ni/ZrO_2-Al_2O_3 however shows a higher surface area but showing a less homogenous dispersion of active phase due to sintering of Zr particles. The catalytic performance of the CO_2 reforming indicates that the Ni/ ZrO_2-Al_2O_3 catalyst shows the best catalytic behaviour. This is closely related to the formation of Ni active sites finely dispersed on the surface of the support induced by the strong nickel oxide, NiO support interaction.

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CHAPTER 1

INTRODUCTION

1.1 Background

Release of carbon dioxide, CO_2 and other greenhouse gases have contributed to global warming. Widespread awareness on global warming spurs activities on finding smart energy solutions. An example of such initiative is to convert the waste CO_2 into valuable environmental-friendly products which fulfils the energy demand of the population. Therefore, CO_2 reforming has received considerable attentions by converting two greenhouse gases, methane, CH4 and CO_2 to valuable synthesis gas (syngas), a mixture of carbon monoxide and hydrogen, (CO and H_2). (Damyanova, Pawelec, Arishtirova, & Fierro, 2012)

This project aims to synthesize catalysts for applications in CO_2 reforming of methane. There has been tremendous interest for the past several years in the catalytic reforming of methane with CO_2 (CO_2 reforming) for the production of CO-rich syngas (ratio of H_2: CO, 1:1). The H_2: CO ratio is lower compared to the conventional steam reforming where a 3:1 ratio is obtained. This offers advantage compared to the established steam reforming process since lower H_2: CO ratio is favourable for Fisher-Tropsch synthesis and many petrochemical processes. In addition, CO_2 reforming is less energy intensive, therefore cheaper compared to the existing steam reforming process.

1.2 Problem Statement

The main issue to be handled in dry reforming is to find a suitable catalyst that would speed up the overall reaction and at the same time is able to prevent net carbon deposition. The catalyst must be able to dissociate CH4 into CHx while at the same time activating CO_2 into CO and O, which will further react with CHx to form CO and H_2. Therefore, the catalyst chosen must be able to have balanced dissociation and activation reactions without the net formation of C. At present, dry reforming process has not been commercialized yet, mainly due to the high deactivation rate from coke deposition and sintering of the nickel-based catalyst. Hence, it is of great interest to develop a coke-free dry reforming catalyst. Therefore, the aim of this project is to obtain optimum performance of the Ni-based catalyst with respect to CO_2 conversion, product yields and selectivity.

1.3 Objectives

The objectives of this project are as follows:

- To develop Ni-based catalysts for dry reforming reaction
- To do the catalyst characterization of the synthesized catalysts
- To evaluate the catalytic performance of catalysts in CO_2 reforming reaction

1.4 Scope of Study

The project aims to develop Ni-based catalysts for CO_2 reforming process by synthesizing via impregnation method on various oxide supports. The nickel-based catalysts will be characterized in terms of particle size, surface area, porosity, phase, surface composition and reducibility properties. The characterization will be done by various microscopic and spectroscopic methods. Then, the activity of the Ni-based catalyst in the CO_2 reforming will be studied in a high-temperature fixed bed microreactor. The dependence of the products composition (H_2:CO ratio) on the catalyst properties will be monitored

CHAPTER 2

LITERATURE REVIEW/THEORY

2.1 CO_2 Reforming of Methane

Methane and carbon dioxide are two greenhouse gases, which gives important implications to the global climatic variations and environmental safety when exposed into the atmosphere. These two gases however can be converted into more valuable synthesis gas (syngas), a mixture of CO and H_2 by using the CO_2 (dry) reforming of methane (Becerra, Dimitrijewits, Arciprete, & Castro Luna, 2001). Although the common processes utilized to generate syngas include steam reforming or partial oxidation, the dry reforming process becomes greatly advantageous as it yields H_2/CO product ratio to 1. This indefinitely shows that dry reforming is suitable for further methanol, oxoalcohols production as well as Fischer-Tropsch synthesis for production of valuable hydrocarbons (Al-Fatesh, Naeem, Fakeeha, & Abasaeed, 2014; Özkara-Aydınoğlu & Aksoylu, 2011).

The dry reforming of methane (Shekhawat, Spivey, & Berry) is shown in equation (1). It is normally accompanied by the formation of carbon as shown in equations (2) and (3).

$$CO_2 + CH_4 \rightarrow 2CO + 2H_2 \qquad \Delta H = 247 \text{ kJ/Mol} \qquad (1)$$

$$CH_4 \rightarrow C + 2H_2 \qquad \Delta H = 75 \text{ kJ/Mol} \qquad (2)$$

$$2CO \rightarrow C + CO_2 \qquad \Delta H = -171 \text{ kJ/Mol} \qquad (3)$$

Although the industrial process has already been developed, suitable catalysts are still awaited. This becomes the major downside of dry reforming. Dry reforming is an endothermic reaction which required high reaction temperature to obtain high conversion levels. High reaction temperature results in coke deposition through the dissociation of methane which may cause catalyst deactivation and clogging of the reactor. Sintering of the metallic phase and support may also occur in a more severe reaction in dry reforming (Galaktionova et al., 2007).

There are two reactions that mainly contributed in coke depostion, methane decomposition and carbon monoxide diporportionantion. Methane decomposition is favoured at high temperatures with lower pressures making it an endothermic reaction whereas CO disporpotionation is favoured at lower temperatures with high pressures making it exothermic in nature. The coke deposition may be reduced by H_2O or O_2 addition to the dry reforming reaction feed. This method has several practical benefits such as syngas produced may have a wider range of H_2/CO by doing adjustment of the CO_2/ H_2O/ O_2 feed ratio (Özkara-Aydınoğlu & Aksoylu, 2011).

However, a significant number of research had been done to resolve the coke deposition problem by developing catalysts, which can obtain balance between rate of surface of carbon formation and the rate of cleaning by surface oxygen, from CO_2 dissociation. One of it includes concentrating in the development of metal catalysts with high catalytic performances towards syngas production and high resistance to carbon deposition for stable long-standing operations. From the study, two lines are investigated. The first is using noble metals (such as Pt, Ru and Rh) which can provide high activity and selectivity to syngas with less sensitivity to carbon deposition. An issue to be handled with noble metals are that they are unsuitable due to high cost and limited availability especially in large-scale commercial use (Arbag, Yasyerli, Yasyerli, Dogu, & Dogu, 2013). With that, another alternative in replacing noble metals are the use of transition metals (like Ni, Fe and Co) as they are more readily available. Although transition metals has given less stability, it is more practical and much more advantageous catalysts from theeconomic point of view (Dimitrijewits, Guraya, Arciprete, Luna, & Becerra, 2001).

2.2 Ni-based catalysts on various oxides supports

The dry reforming reaction has been studied over numerous supported catalysts, especially on the Ni-based catalysts. This is due to its higher reactivity, readily available, and lower price compared with that of noble metals, nickel (Ni) is the most frequently reported metal in dry reforming of methane. Again, Ni-based catalysts deactivate easily due to carbon deposition and sintering of metal phase or support (Dimitrijewits et al., 2001). Therefore, many research groups have aimed on improving the activity and stability of Ni such as changing the nature of the support, selecting different supports (Becerra et al., 2001; Özkara-Aydınoğlu & Aksoylu, 2011), catalyst preparation method and the addition of promoters into catalyst formation.

Ni-based catalysts with supports like Al_2O_3 and SiO_2 have been widely investigated for the dry methane reforming. Ni/Al_2O_3 and Ni/SiO_2 prepared by impregnation had high initial conversions but deactivated with time due to carbon deposition or sintering. Modifications have been studied to improve the performance of Ni/Al_2O_3 and Ni/SiO_2 catalysts (Therdthianwong & Siangchin, 2008; Pan, Liu & Shi, 2008). To further achieve high levels of CH_4 and CO_2 conversions with minimized carbon deposition , modification can be done by adding small amounts of noble metals (such as Pt, Ru and Rh) have been investigated. When Ni/a- Al_2O_3 and Ni/SiO_2 catalysts doped with a small amount of Rh, dry methane reforming showed a higher activity than the unpromoted Ni catalysts. The addition of Ru or Pd to Ni/ SiO_2 also strongly enhanced the activity and stability of the catalyst in dry reforming (Hou & Yashima, 2003; Jozwiak, Nowosielska & Rynkowski, 2005).

Another literature search has led to the conclusion that $Ni/MgAl_2O_4$ has proven to give higher metal dispersion for coke-free reforming catalyst due to the strong interaction between Ni oxide species and $MgAl_2O_4$ supports. From the study, it is determined that the catalytic performance of Ni-based catalysts in the dry reforming of methane depends greatly on the kind of support (Damyanova et al., 2012).

Other supports such as zirconia, ZrO_2 are known to separate metal-support interactions to enhance catalytic performances, due to the oxygen storage/transport characteristics of support caused by the high lattice oxygen mobility and to the generation of active centres at the interface between metal and support (Pawelec, Castaso, Arandes, Bilbao, Thoma & Pesa, 2007). Among other catalyst supports, ZrO_2 is a promising candidate due to its ability to improve the stability of the catalyst under both oxidizing and reducing atmospheres. It has been reported that zirconia can prevent coke formation in reforming processes such as the dry reforming of methane. From a study by Rahemi et al. 2013, the nano-sized and high dispersion of the Ni particles in a plasma-treated $Ni/Al_2O_3–ZrO_2$ nanocatalyst is confirmed by the physicochemical characterizations of synthesized nanocatalysts. The high activity of plasma-treated $Ni/Al_2O_3–ZrO_2$ nanocatalyst in methane dry reforming is obtained with a higher surface area, smaller size, and higher dispersion of Ni particles. Therefore, the ZrO_2 and their interaction with Al_2O_3 due to plasma discharge makes it a more stable catalyst against coke deposition. However, despite that plasma can create more active and stable catalysts in methane dry reforming, the high energy consumption and expensive equipment makes it unreliable for application in industry (Rahemi, Haghighi, Babaluo, Jafari, & Estifaee, 2013).

2.3 Techniques for Catalyst Preparation

Table 1: Techniques for Catalyst Preparation

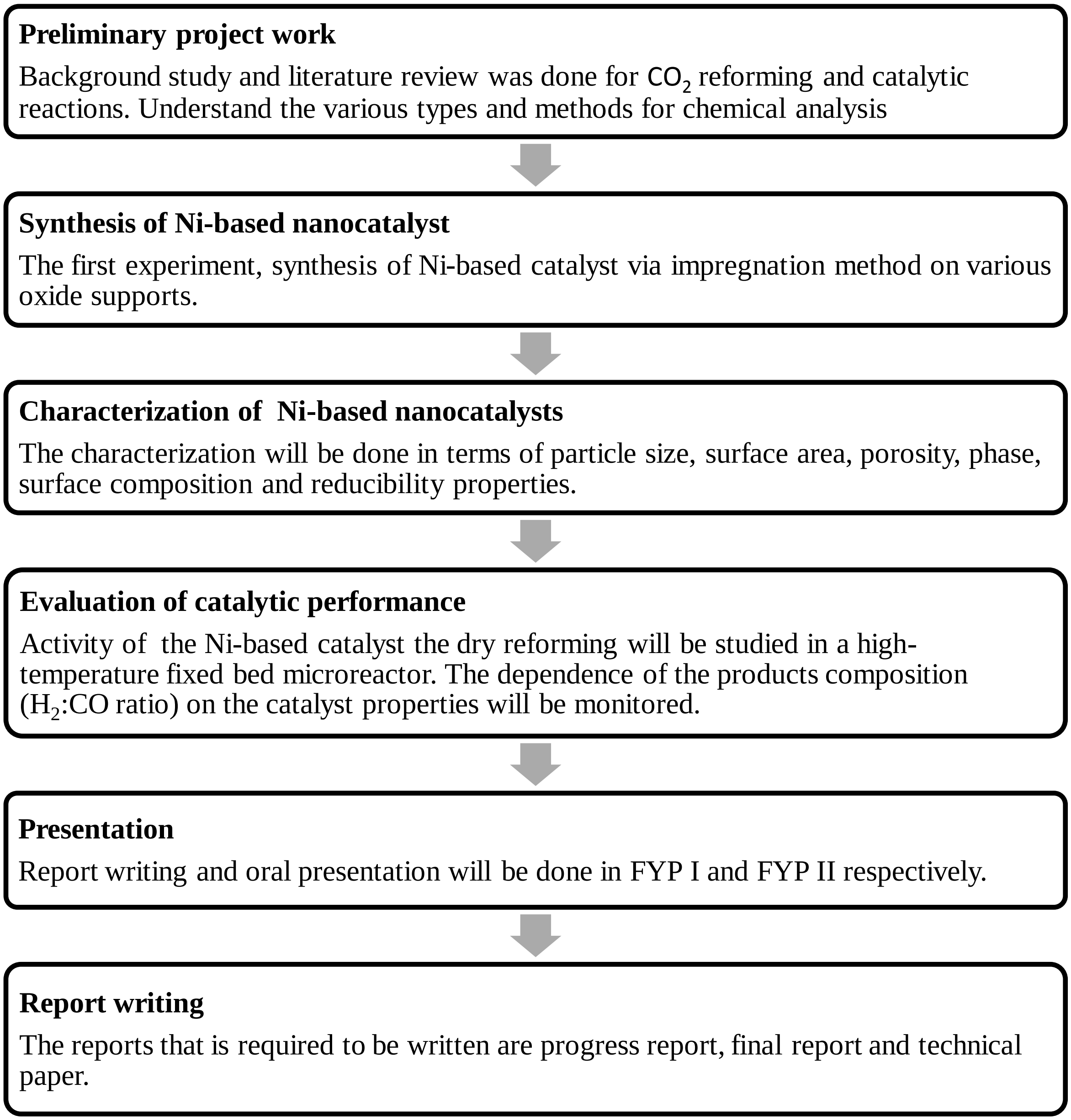
Author	Catalyst	Techniques	Analysis
(Damyanova, Pawelec, Arishtirova, & Fierro, 2012)	Nickel-based Ni/δ, θ-Al_2O_3 Ni/$MgAl_2O_4$ Ni/SiO_2-Al_2O_3 Ni/ZrO_2-Al_2O_3	via impregnation	Ni catalyst supported on $MgAl_2O_4$ (Ni/$MgAl_2O_4$) - Shows the best catalytic behavior. - Smallest average size of metallic Ni particles (5.1nm) - absence of filamentous carbon - Strong reaction retards metal Ni sintering and coke formation.
(Guo, Lou, Zhao, Chai, & Zheng, 2004)	Nickel-based Ni/γ- Al_2O_3 Ni/MgO-Al_2O_4 Ni/$MgAl_2O_4$	via wet-impregnation	Ni catalyst supported on $MgAl_2O_4$ (Ni/$MgAl_2O_4$) - exhibits stable performance - no NiO crystalline phase detected - small Ni particle sizes, little sintering occurred.
(Therdthianwong, Siangchin, & Therdthianwong, 2008)	Nickel-based Ni/ Al_2O_3 Ni/ZrO_2-Al_2O_3	via impregnation	Ni catalyst supported on ZrO_2-Al_2O_3 (Ni/ZrO_2-Al_2O_3) - higher surface area, smaller size of Ni particles - higher dispersion of Ni particles - interaction between ZrO_2 and Al_2O_3 makes it more stable against coke deposition
(Özkara-Aydınoğlu & Aksoylu, 2011)	Pt-Ni (bimetallic) Pt-Ni/δ-Al_2O_3 (different ratio)	via impregnation	Lowest Pt-Ni ratio: - exhibits highest catalytic activity and stability - led to easy reduction of nickel oxide species - smaller nano-sized nickel particles yielding better dispersion

Author	Catalyst	Techniques	Analysis
(Alipour, Rezaei, & Meshkani, 2014)	Ni-based Ni/Al_2O_3 $Ni/MgO-Al_2O_3$ $Ni/CaO-Al_2O_3$ $Ni/BaO-Al_2O_3$	via sol-gel method	- addition of MgO, CaO and BaO improved catalytic activity and decreased coke formation Ni catalyst supported on $MgO-Al_2O_3$ ($Ni/MgO-Al_2O_3$) - found to be the best modifier for Ni/Al_2O_3 because of $MgAl_2O_4$
(Rahemi, Haghighi, Babaluo, Jafari, & Khorram, 2013)	Ni-based Ni/Al_2O_3 $Ni/Cu-Al_2O_3$ $Ni/ Co-Al_2O_3$	via co-impregnation method modified by non-thermal plasma	Ni catalyst supported on $Co-Al_2O_3$ ($Ni/Co-Al_2O_3$) - has a uniform morphology and a better dispering of active sites - big crystals of CuO - aggregation of of small Ni are preventedd by adding cobalt into Ni-based catalyst - it has better activity of the reactants conversion and also in CO and H_2 production - did not undergo any deactivation.
(Damyanova et al., 2012)	Ni-based $Ni/ Ni/Al_2O_3$ $Ni/SiO_2- Al_2O_3$ $Ni/ZrO_2- Al_2O_3$ $Ni/MgAl_2O_4$	via plazma method	Ni catalyst supported on $MgAl_2O_4$ ($Ni/MgAl_2O_4$) - Shows the best catalytic behavior. - Smallest average size of metallic Ni particles (5.1nm) - absence of filamentous carbon - Strong reaction retards metal Ni sintering and coke formation.

CHAPTER 3

METHODOLOGY/PROJECT WORK

3.1 Project Flowchart



Preliminary project work

Background study and literature review was done for CO_2 reforming and catalytic reactions. Understand the various types and methods for chemical analysis

Synthesis of Ni-based nanocatalyst

The first experiment, synthesis of Ni-based catalyst via impregnation method on various oxide supports.

Characterization of Ni-based nanocatalysts

The characterization will be done in terms of particle size, surface area, porosity, phase, surface composition and reducibility properties.

Evaluation of catalytic performance

Activity of the Ni-based catalyst the dry reforming will be studied in a high-temperature fixed bed microreactor. The dependence of the products composition (H_2:CO ratio) on the catalyst properties will be monitored.

Presentation

Report writing and oral presentation will be done in FYP I and FYP II respectively.

Report writing

The reports that is required to be written are progress report, final report and technical paper.

Figure 1: Project Flow Chart

The flow of the methodology goes as the above flow chart. Throughout the research process, preparation for the experimental work will also be done in order to save time and finish the project within the given time period. The equipment and the materials are ordered and will be set to meet the demands of the project.

3.2 Materials and Equipments

This project is using nickel nitrate solution, Ni $(NO_3)_2.6H_2O$ for the synthesis of Ni-catalysts by impregnation method. Aluminium oxides powders (γ- Al_2O_3, ZrO_2-Al_2O_3, MgO-Al_2O_3) are used as supports for catalysts preparation.

Table 2: Chemicals and oxides supports required for catalyst synthesizing

MATERIALS	COMPOSITIONS
Nickel nitrate aqueous solution, $Ni(NO_3)_2.6H_2O$	Ni loading 1. 9 wt%
Alumina (Al_2O_3) Supplier: SASOL, Germany Specific surface area: 238 m^2/g Loose bulk density: 0.65 g/ml	
Magnesium aluminate oxide, (Al_2O_3-MgO) Supplier: SASOL, Germany Specific surface area: 1. 30% wt MgO – 109 m^2/g 2. 70% wt MgO – 185 m^2/g Loose bulk density: 1. 30% wt MgO – 0.35 g/ml 2. 70% wt MgO – 0.32 g/ml	1. Al_2O_3 = 71.2 wt%, MgO = 28.8 wt% 2. Al_2O_3 = 30.9 wt%, MgO = 69.1 wt%
Zirconia aluminate oxide, (Al_2O_3-ZrO_2) Supplier: SASOL, Germany Specific surface area: 211m^2/g Loose bulk density: 0.66 g/ml	1. Al_2O_3 = 80.4 wt%, ZrO_2 = 19.6 wt%

The synthesized catalysts are characterized in several aspects using its respective chemical analysis which are:

Table 3: Chemical Analysis for synthesized catalyst

Characteristic	Chemical Analysis
Particle size and its distribution	Transmission electron microscope (TEM)
Crystallite phases	X-ray Diffraction (XRD)
Textural properties (surface area)	Brunauer–Emmett–Teller (BET)
Catalyst morphology and elemental composition	- Field emission scanning electron microscope (FESEM)
Catalyst morphology and elemental composition	Energy dispersive X-ray (EDX)

Then, the activity of the Ni-based catalyst in the CO_2 reforming is studied in a high-temperature fixed bed micro-reactivity reactor.

Figure 2: Micro-reactivity reactor used for reaction studies

Figure 3: On-line gas chromatography

The reactor used is an automated and computer-controlled reactor for catalytic microactivity tests. It is a fully automated system with real time results, quasi zero dead volume, high stability and accuracy. The reactor is also attached to an on-line gas chromatography as it eases the analysis of reaction done in the reactor. The reactor configuration is as follows:

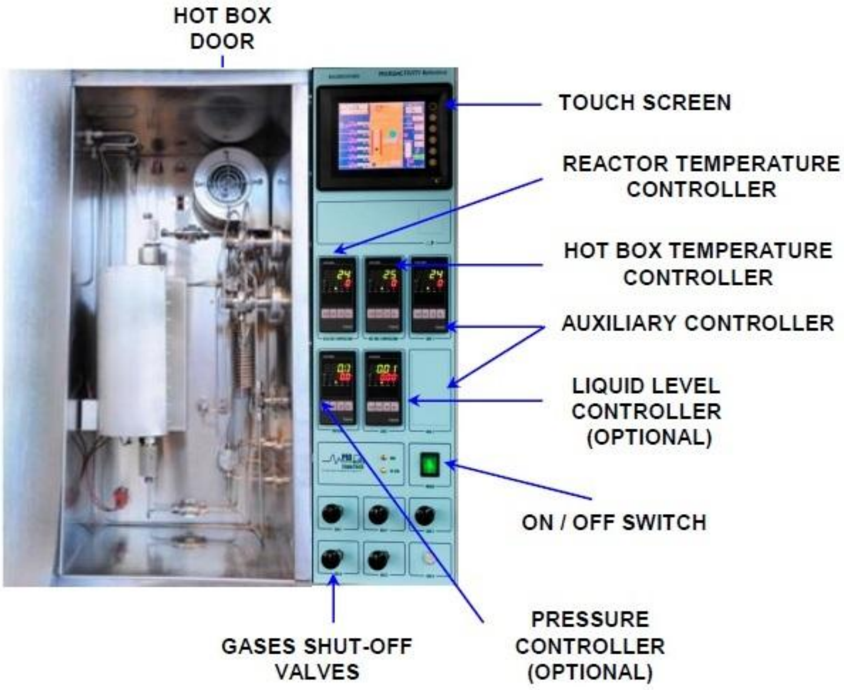


Figure 4: Reactor configuration

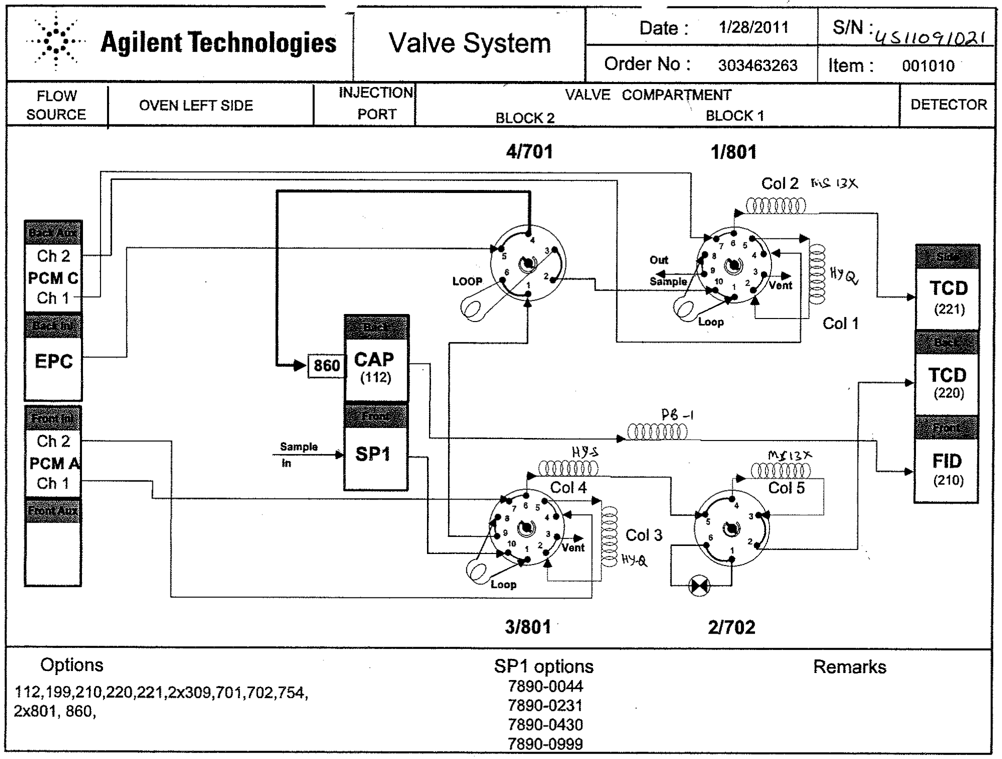
Model: *Automated Microreactor universal system with high performance and repetitiveness (*WO-2006008328/EP-1757930/US-2008063565)

Internal volume: 20 mL

Maximum working conditions: P = 100 bar @ 650 °C SS316

Maximum reactor pressure: 1304 bar at 37 °C; 400 bar at 482 °C

Reactants and products were analyzed by means of on-line gas chromatography equipped with TCD and FID controller. The schematic diagram of the configuration for GC system is illustrated in Figure 5.



Agilent Technologies | Valve System

Date : 1/28/2011

S/N : 4S11091021

Order No : 303463263

Item : 001010

Options

112,199,210,220,221,2x309,701,702,754,
2x801, 860,

SP1 options

7890-0044
7890-0231
7890-0430
7890-0999

Remarks

Figure 5: GC valve system

3.3 Project Procedure

3.3.1 Catalyst Preparation

Aluminium oxides powders (γ- Al_2O_3, ZrO_2-Al_2O_3, MgO-Al_2O_3) used as supports, provided by SASOL for catalysts are already available in lab for catalyst preparation. The Ni-catalysts was synthesized by impregnation method using aqueous precursor solution of $Ni(NO_3)_2.6H_2O$ which was prepared as the standard solution. The standard solution, $Ni(NO_3)_2.6H_2O$ solution is prepared in a volumetric flask where 250 ml of deionized water is poured into $Ni(NO_3)_2$.

The samples were dried and calcined at 100°C and 550°C for 12 and 4 hours respectively (Özkara-Aydınoğlu & Aksoylu, 2011). A drying oven was used to dry the synthesized catalysts. As for the calcination, a tube furnace was used. The samples were put into rectangular ceramic container and were purged with Argon gas for 1 hour in the tube furnace before being calcined.

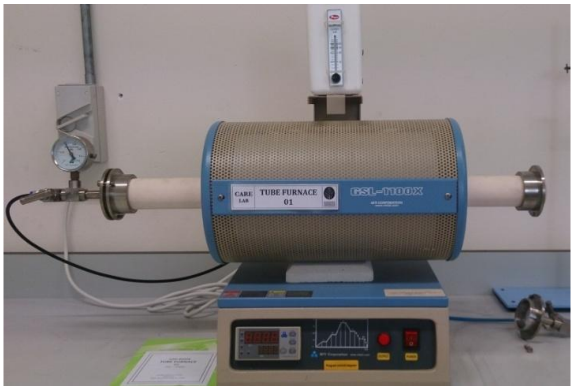


Figure 6: Tube furnace for calcination

The proposed theoretical Ni content is 9 wt%. Samples are labelled as:

1. Ni/Al (Ni/γ- Al_2O_3)
2. Ni/MgAl-1 (Ni/MgO-Al_2O_3 with MgO = 30 wt %),
3. Ni/MgAl-2 (Ni/MgO-Al_2O_3 with MgO = 70 wt %)
4. Ni/ZrAl (Ni/ZrO-Al_2O_3).

Each of the samples prepared was 5 gram each. Figure below shows a summary of the procedure for catalyst preparation:

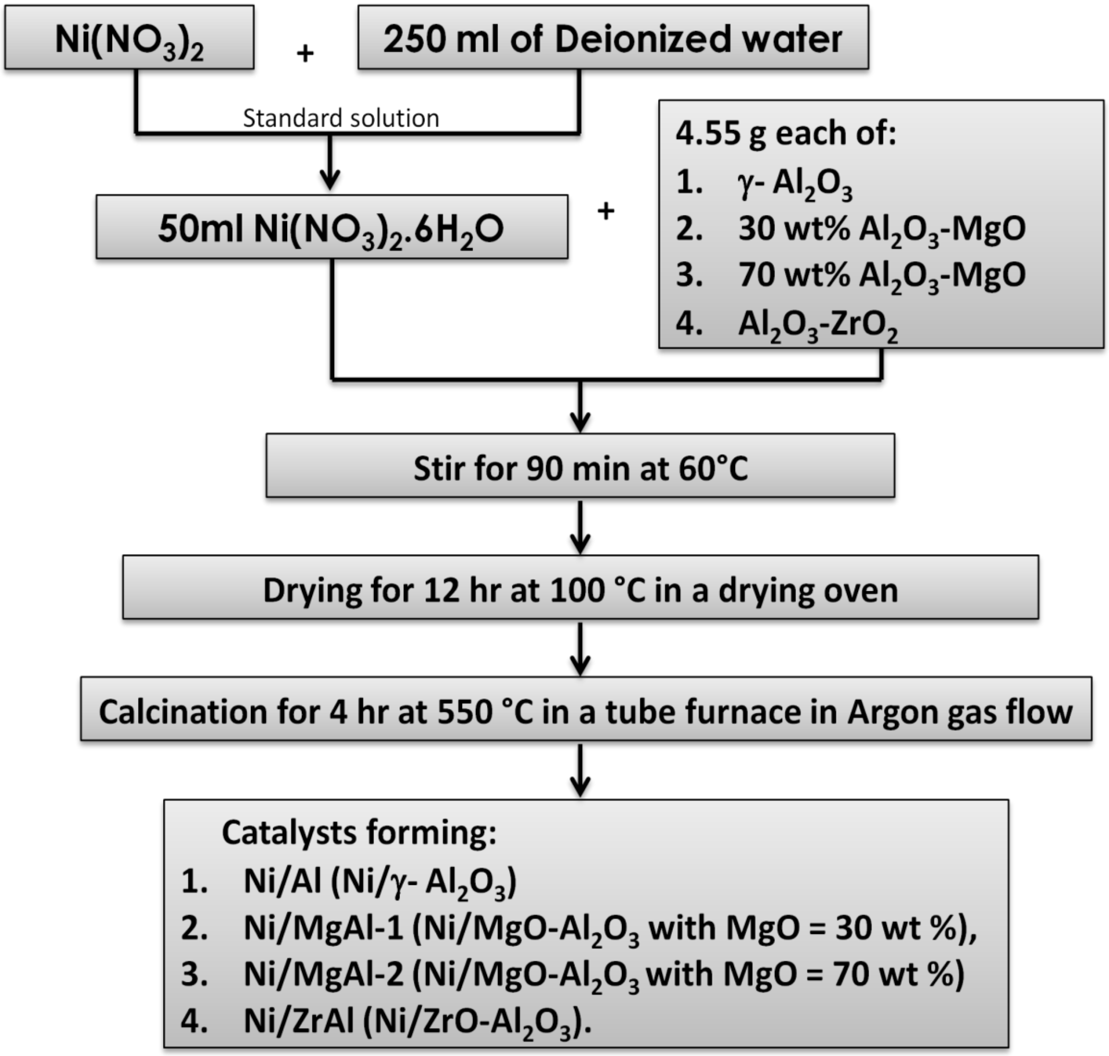


Figure 7: Process flow for synthesis of catalysts

3.3.2 Activity Measurements

The catalytic experiments in the reaction of CH_4 reforming with CO_2 were conducted at high-pressure fixed bed micro reactor located in the Catalytic Reaction (CARE) Lab. The activity of supported catalysts: $Ni/MgO\text{-}Al_2O_3$ and $Ni/ZrO\text{-}Al_2O_3$ were tested at high temperature with equimolar CH_4 and CO_2 mixture without using inert gases as diluents.

The reaction conditions are as follows:

Table 4: Reaction conditions for CO2 Reforming of Methane

Parameters	Details
Temperature	- Prior to the reaction, the catalysts were reduced in situ at 600°C for 4 hr in H_2 flow (20ml/min) and cooled to 550°C, after being purged for 1 hour using Helium gas. - After reactant gas feed (containing CH_4 and CO_2), activity tests performed from at 650°C. Readings of data of the components are taken at intervals of 30 min for 5 hours
Catalyst:	0.2 g each
Total time run in reactor:	5 hours
Pressure	Atmospheric
CH_4: CO_2 ratio	1:1
Feed Flow rate	30ml/min (15ml/min for CH_4; 1 ml/min for CO_2)
Reactant and product Analysis	Gas Chromatograph (on-line)

From the reaction, the conversion of both reactant CH_4 and CO_2 and selectivity of the product CO and H_2 were determined from the data obtained from the gas chromatography by calculations according to the following formulas:

$$X_{CH_4}\,\% = \frac{C_{CH_{4,in}} - C_{CH_{4,out}}}{C_{CH_{4,in}}} \times 100$$

$$X_{CO_2}\,\% = \frac{C_{CO_{2,in}} - C_{CO_{2,out}}}{C_{CO_{2,in}}} \times 100$$

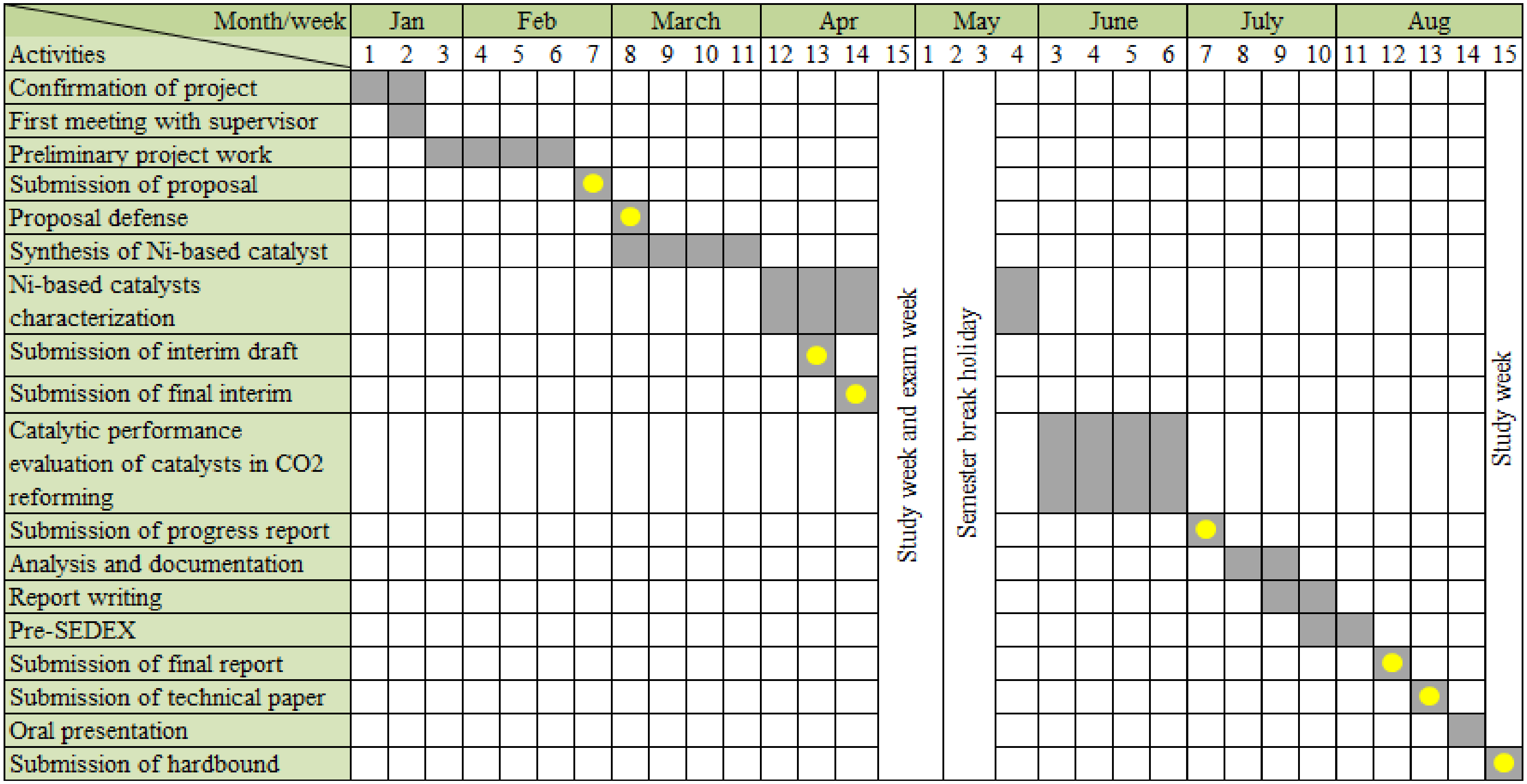
$$Y_{H_2}\,\% = \frac{C_{H_{2,net}} - C_{H_{2,blank}}}{\left(C_{H_{2,net}} - C_{H_{2,blank}}\right) + C_{CO}} \times 100$$

$$Y_{CO}\,\% = \frac{C_{CO}}{\left(C_{H_{2,net}} - C_{H_{2,blank}}\right) + C_{CO}} \times 100$$

where X_i and Y_i are conversion of reactants and selectivity of products, respectively. $C_{i,in}$ is the initial molar fraction of component i in the feed, and $C_{i,out}$ is the final molar fraction of component i in the product stream.

3.4 Project Timeline

The Gantt chart for entire project including FYP I and FYP II are planned and shown in figure below.



Month/week	Jan			Feb				March				Apr				May				June				July				Aug				
Activities	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	1	2	3	4	3	4	5	6	7	8	9	10	11	12	13	14	15
Confirmation of project	■	■													Study week and exam week		Semester break holiday															Study week
First meeting with supervisor		■																														
Preliminary project work			■	■	■	■																										
Submission of proposal							●																									
Proposal defense								●																								
Synthesis of Ni-based catalyst								■	■	■	■																					
Ni-based catalysts characterization												■	■	■					■													
Submission of interim draft													●																			
Submission of final interim														●																		
Catalytic performance evaluation of catalysts in CO2 reforming																				■	■	■	■									
Submission of progress report																								●								
Analysis and documentation																									■	■						
Report writing																										■	■					
Pre-SEDEX																											■	■				
Submission of final report																													●			
Submission of technical paper																														●		
Oral presentation																															■	
Submission of hardbound																																●

Key milestones are indicated in the yellow dotted symbol.

Figure 8: Gantt chart for the entire project

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization

Characterization of the catalysts is done to examine and determine the specific characteristics of the catalysts. The catalysts synthesized are characterized in terms of particle size, surface area, crystallite phases, and catalysts morphology and reducibility properties. The characterization is done using suitable equipments according to the properties that needed to be analyzed.

4.1.1 Textural properties (BET) of catalysts

Structural properties of the modified nickel catalysts with MgO and ZrO_2 with 9wt% of Ni are presented in Table 5.

Table 5: Textural properties of catalysts

Catalyst	Labelled as	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
Ni/Al_2O_3	Ni/Al	167.7	0.4	10.2
Ni/ZrO_2-Al_2O_3	Ni/ZrAl	153.3	0.3	8.3
Ni/30%MgO-Al_2O_3	Ni/MgAl-1	113.5	0.4	14.4
Ni/70%MgO-Al_2O_3	Ni/MgAl-2	99.7	0.5	18.8

*calculated by the BET equation

As can be seen, the catalyst supported by ZrO_2, Ni/ZrAl possessed higher specific surface area while the catalyst with a larger weight percentage of MgO, Ni/MgAl-2 gives out the smallest surface area. The surface areas of supported catalysts are dominantly controlled by the surface area of the support. However, for the pore size Ni/ZrAl possessed the smallest size whilst the Ni/MgAl-2 has the largest pore size.

Isotherm Linear Plot

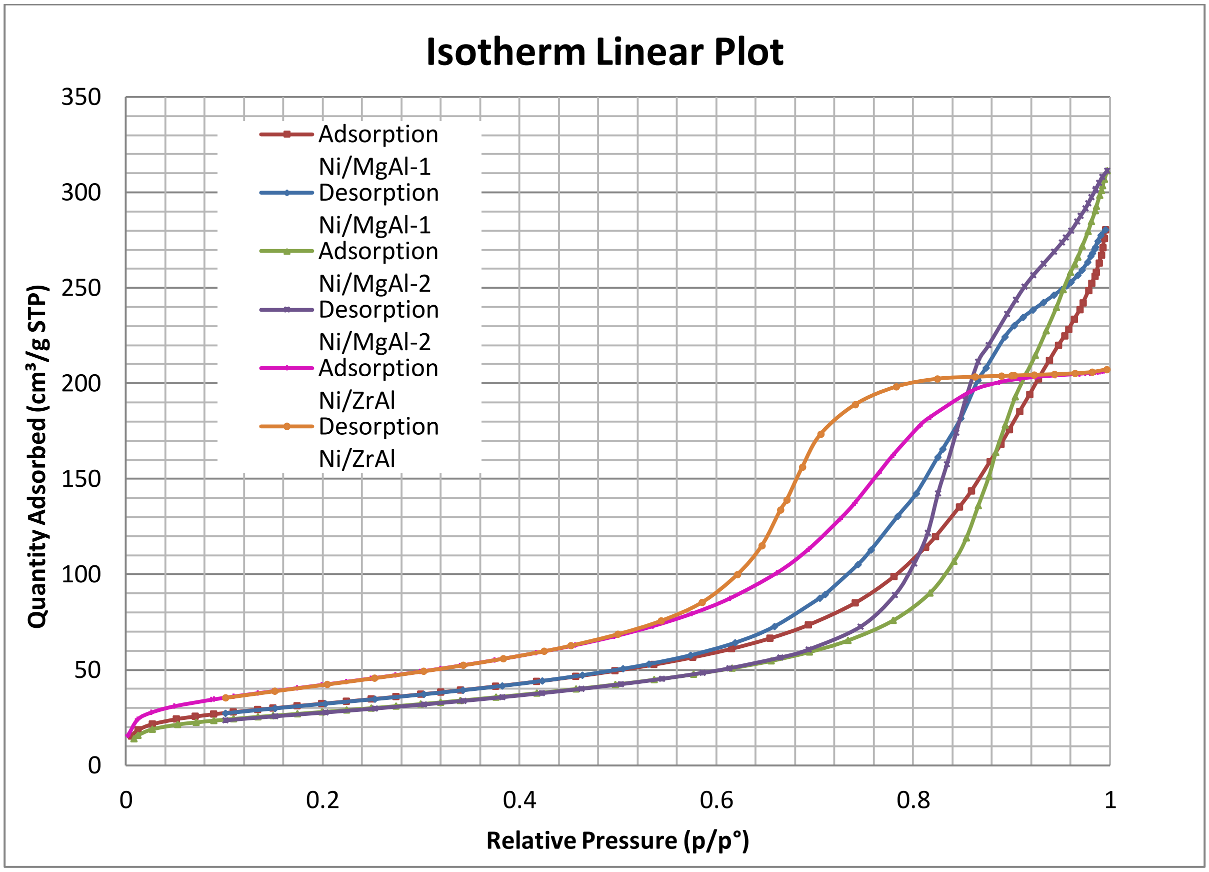


Figure 9: N_2 adsorption/desorption isotherms

Figure 8 shows the nitrogen adsorption/desorption isotherms. For all the samples, the isotherms can be classified as a type IV isotherm, also known as mesoporous materials. According to International Union of Pure and Applied Chemistry (IUPAC) classification, the hysteresis loop is type H2 in this case pores can have non uniform size or shape (Leofanti, G et al).

4.1.2 FESEM Analysis

To identify the catalysts morphology, Field emission scanning electron microscope (FESEM) analysis was done for all synthesized catalysts. The FESEM analysis was done in a Variable Pressure FESEM (Zeiss Supra5 VP).

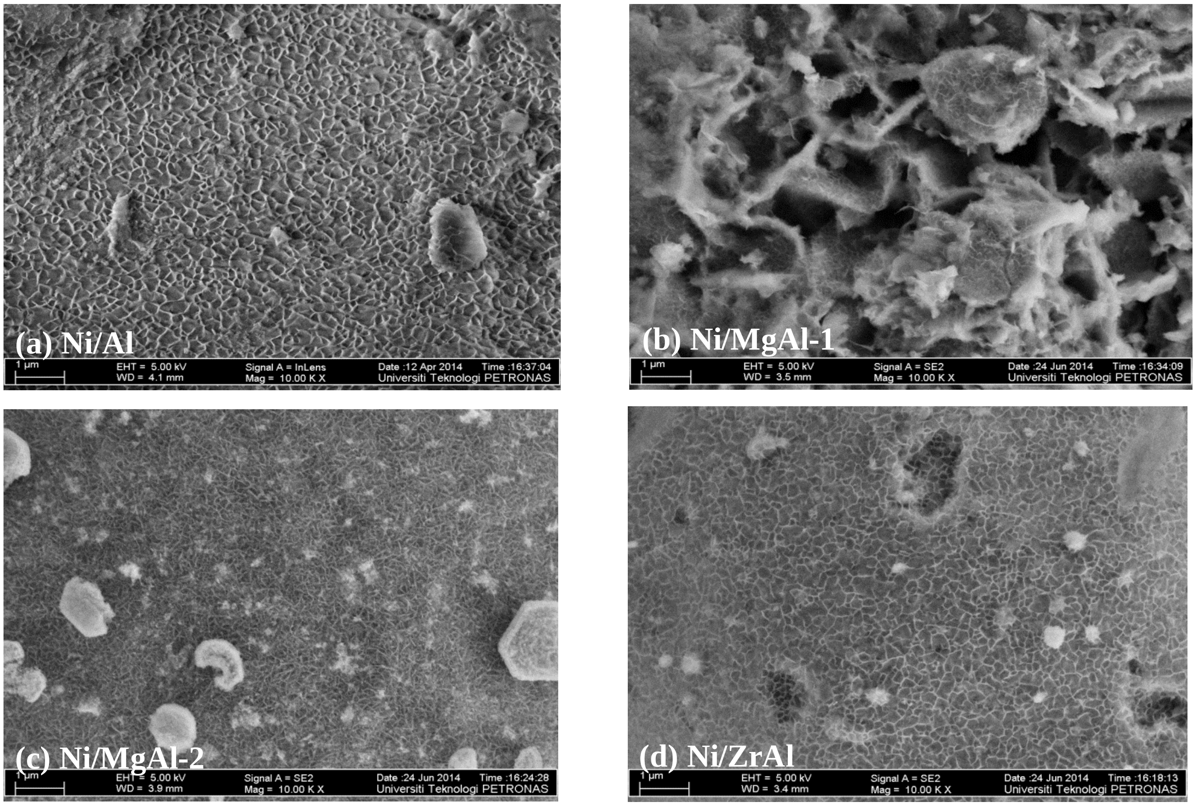
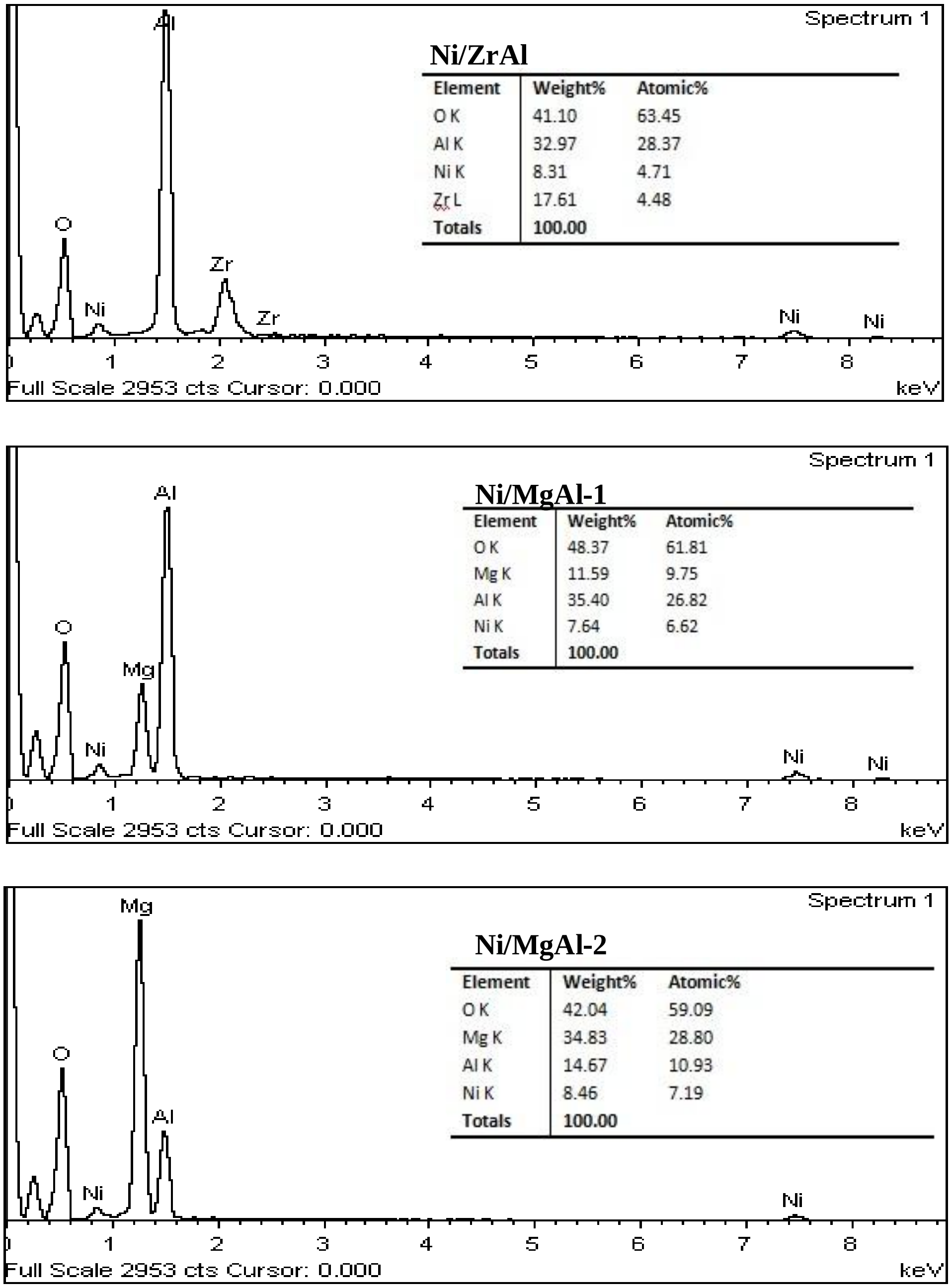


Figure 10: Micrographs of (a) Ni/Al, (b) Ni/MgAl-1 (c) Ni/MgAl-2 and (d) Ni/ZrAl

Comparisons are made between all the catalysts. All catalysts show slight corrugated forms. As can be seen, the surfaces of Ni/MgAl-2 and Ni/ZrAl have a similar appearance with the Ni/Al. From the micrograph of MgO sample with lower wt%, catalysts particles, Ni/MgAl-1 were large and the surface was comparatively rough. In contrast, both samples with Ni/ZrAl and Ni/MgAl-2 have more uniform surfaces and smaller particles, indicating presence of supports decreased particle size. In comparison between different weights percent of MgO, with more MgO present in the catalysts, the catalysts improved in terms of its morphology and particle size.

4.1.3 Energy dispersive X-ray (EDX)

Similar to FESEM, EDX analysis is conducted to determine the residing components in the sample.



Ni/ZrAl

Element	Weight%	Atomic%
O K	41.10	63.45
Al K	32.97	28.37
Ni K	8.31	4.71
Zr L	17.61	4.48
Totals	**100.00**	

Ni/MgAl-1

Element	Weight%	Atomic%
O K	48.37	61.81
Mg K	11.59	9.75
Al K	35.40	26.82
Ni K	7.64	6.62
Totals	**100.00**	

Ni/MgAl-2

Element	Weight%	Atomic%
O K	42.04	59.09
Mg K	34.83	28.80
Al K	14.67	10.93
Ni K	8.46	7.19
Totals	**100.00**	

Figure 11: EDX analysis (a) Ni/ZrAl, (b) Ni/MgAl-1 and (c) Ni/MgAl-2

From EDX analysis of Ni/ZrAl and Ni/MgAl-1, well dispersion of Ni particles can be concluded. Ni and Zr in Ni/ZrAl catalysts also have a good dispersion. EDX pictures show dispersion in micro scale, all particles (Ni, Zr and Mg) are well dispersed in Ni/ZrAl and Ni/MgAl-1 catalysts. However, in Ni/MgAl-2 did not exhibit the same dispersion. This is may be because of some error happened during the catalyst preparation or during the EDX analysis preparation. Among the two factors cannot be confirmed as to which is the main reason for it.

4.1.4 X-ray Diffraction (XRD)

XRD is the scattering of X-rays by the regularly spaced atoms of a crystal, useful in obtaining information about the structure of the crystal. The XRD for the samples are done in a Bruker D8 Advance with 2000 steps with time of 2s at every interval and scan axis of 2-theta. XRD patterns of the calcined catalysts with supports are shown in Figure 12.

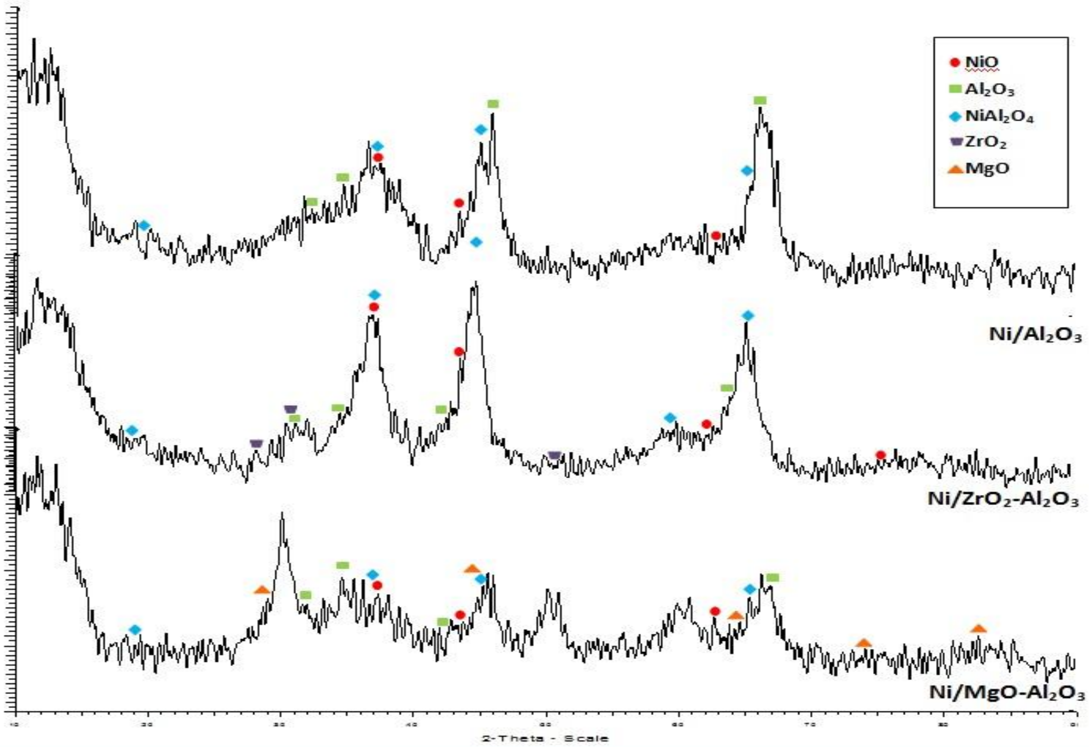
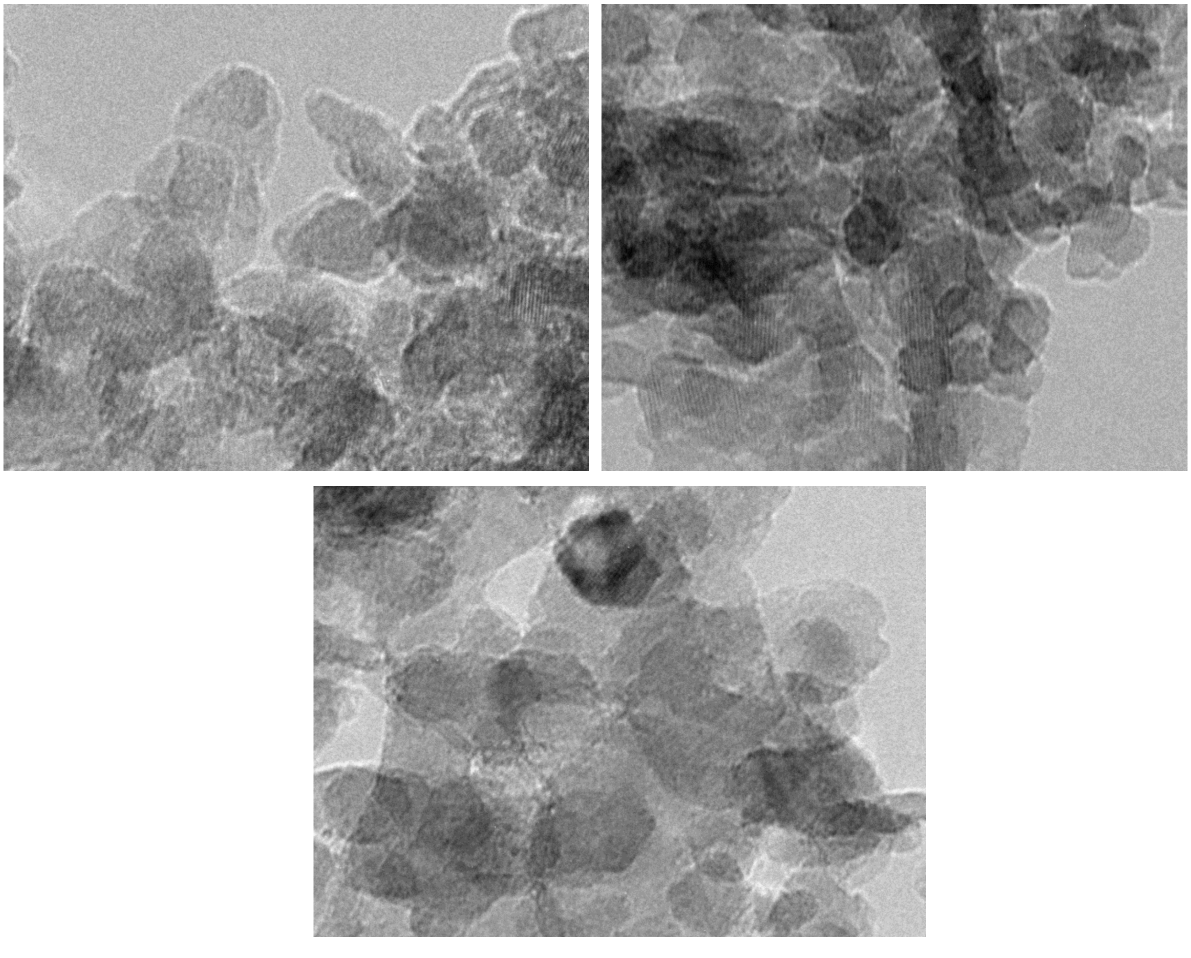


Figure 12: XRD patterns of (a) Ni/Al, (b) Ni/ZrAl and (c) Ni/MgAl

Phase composition of the Ni/Al, Ni/ZrAl and Ni/MgAl catalysts were analyzed by XRD patters shown in the figure. The presence of Ni in the form of NiO is clear but most of $NiAl_2O_4$ attributed peaks overlap with other peaks. NiO and NiAl2O4 crystallites are very small in all three samples as the related peaks are quite broad. The observed NiO and $NiAl_2O_4$ peaks are very broad indicating thereby good dispersion of particles of NiO and NiAl2O4 crystallites on Al_2O_3 support. MgO has weak and broad peaks, well dispersed in catalysts. On contrary, ZrO_2 in Ni/ZrAl has sharper peaks resulting in bigger crystallites of ZrO_2. Sintering most likely happens to ZrO_2 due to high temperature of calcination.

4.1.5 Transmission Electron Microscope (TEM)

TEM are used to analyze the samples particle sizes and its distributions and the observations were performed on a Zeiss Libra 200 system. The catalysts was dispersed ultrasonically in ethanol and deposited on a TEM grid. TEM micrographs of Ni/ZrAl, Ni-MgAl-1 and Ni/MgAl-2 were illustrated in Figure 12.



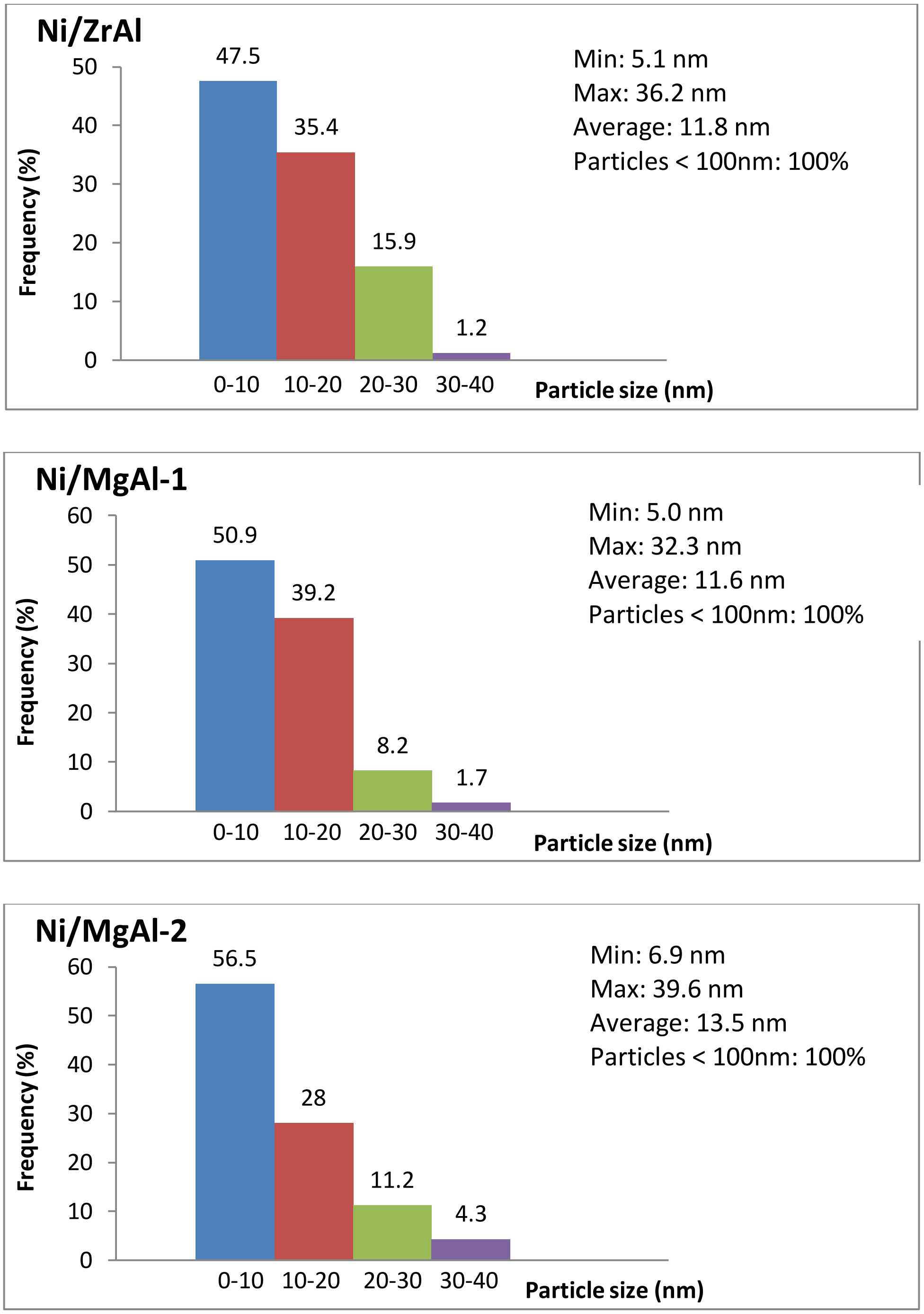


Figure 13: TEM micrographs and particle size histogram of (a) Ni/ZrAl, (b) Ni/MgAl-1 and (c) Ni/MgAl-2

TEM micrographs of Ni/ZrAl, Ni/MgAl-1 and Ni/MgAl-2 were illustrated in figure above. Minimum and maximum Ni particle size in Ni/ZrAl was 5.1 nm and 36.2 nm, respectively. The average Ni particle size was 11.8 nm and all Ni particles sizes were in less than 100 nm region. Based on the TEM micrographs, there is slight crystallinity in active phase in

Ni/ZrAl catalyst. Minimum and maximum Ni particle size in Ni/MgAl-l was 5.0 nm and 32.3 nm, respectively. The average Ni particle size was 11.6 nm and all Ni particles sizes were in less than 100 nm region. Broad dispersion of active phase in Ni/MgAl-1 particles can be observed. Average particle size in Ni/MgAl-2 catalyst is 13.5 nm that was relatively high than other catalysts. Based on the TEM micrographs, the crystallinity in active phase in both Ni/MgAl catalysts are quite visible.

4.2 Catalytic Performance Study of CO_2 Reforming of Methane

The activity of supported Ni-based catalysts: Ni/ZrO_2-Al_2O_3, Ni/MgO-Al_2O_3, was tested at 650°C with equimolar CH_4 and CO_2 mixture without using inert gases as diluents.

Blank Run on Catalyst

However during the initial stage of the reaction, some problems were encountered during the reaction. There was presence of high content of Hydrogen, H_2 at the beginning of the reaction. The reason for this to happen is still under investigation. To reduce the amount of H_2, a blank run on the catalyst had been done. Below are the conditions of the blank run on catalyst reaction:

Table 6: Blank run conditions

Parameters	Details
Flow rate	30 ml/min
Type of catalyst	Ni/ZrAl
Weight of catalyst	0.2 g
Total time in reactor	5 hours
Purging time	1 hour

Based on the blank run, the amount H_2 obtained was determined and taken as reference to calculate the actual amount of H_2 produced in the CO_2 reforming reaction with CH_4 and CO_2 as reactant. Amount of H_2 used in the calculations is 1031.66.

The catalytic properties of the supported Ni-based catalysts are summarized in Table 7.

Table 7: Catalyst properties during CO_2 reforming of methane reaction

Sample	**CH_4 conversion (%)**	**CO_2 conversion (%)**	**H_2 selectivity (%)**	**CO selectivity (%)**	**H_2/CO**
Ni/ZrAl	12.8	28.9	68.8	31.3	2.2
Ni/MgAl	28.3	36.3	92.4	7.6	12.2

* Time = 300 min; T = 650°C; $CH_4/CO_2 = 1$;

The values of CH_4 and CO_2 conversions, as well as CO and H_2 yields are taken at steady state activity. The highest CH_4 (28.3%) and CO_2 (36.3%) conversions at 300 min are achieved for Ni/MgAl catalyst. Ni-based catalyst supported on Ni/ZrAl shows comparable values of CH_4 (12.8%) and CO_2 (28.9%). It should be noted that the CH_4 conversion values for all catalysts are lower than those of CO_2 conversion because the production of synthesis gas from CO_2 reforming with methane is probably influenced by the occurrence of the reverse water-gas shift reaction. Reverse water-gas shift reaction would produce water in the reaction products. Moreover, the product side of the reaction resulting in higher yield of H_2 than that of CO caused by the consumption of CO and dissociation of CO_2 to H_2 which occurs under experimental conditions. Both facts lead to a molar ratio of H_2/CO more than unity. Maximum H_2 (94.4%) and CO (7.3%) yields are obtained over Ni/ZrAl sample followed by Ni/MgAl respectively.

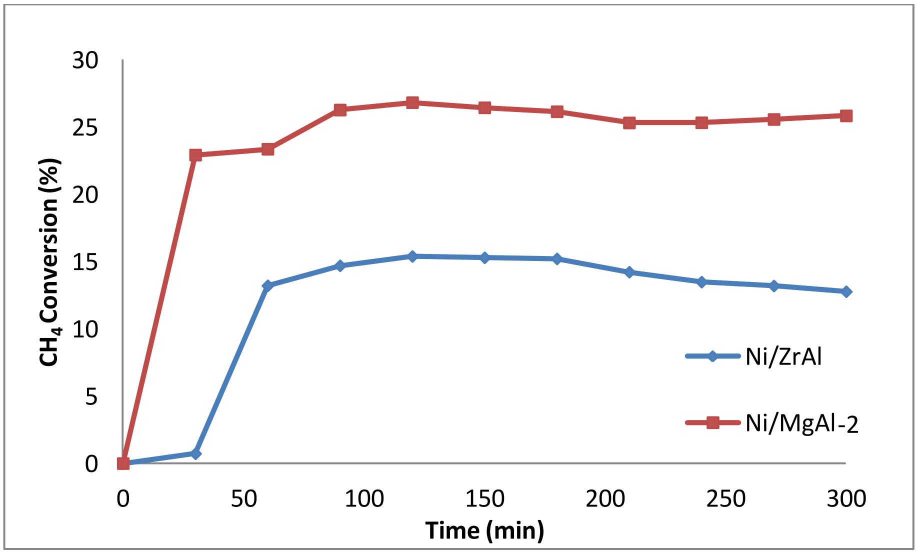


Figure 14: CH_4 conversion (%) on time-on-stream

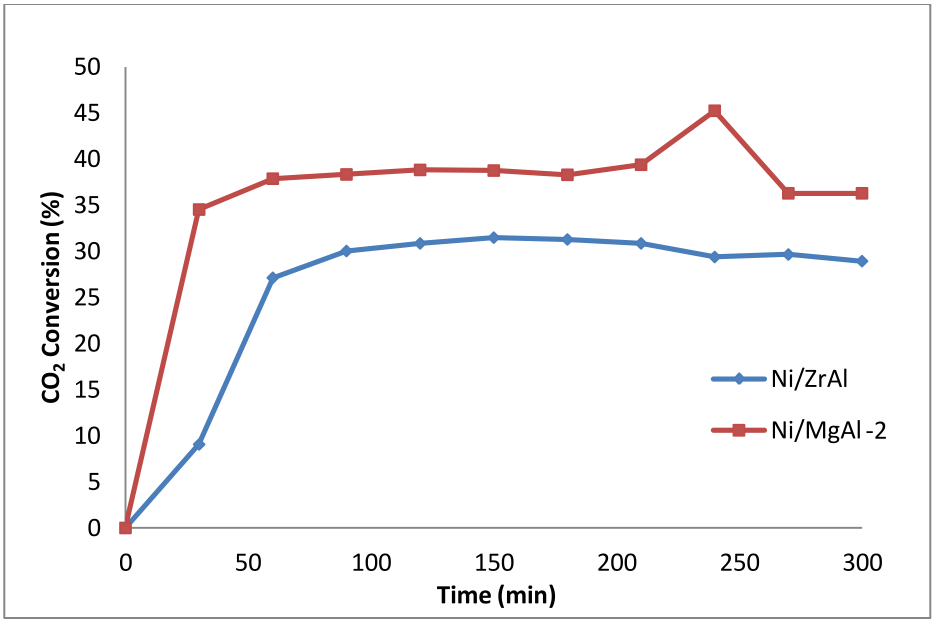


Figure 15: CO_2 conversion (%) on time-on-stream

It is well known that the catalysts during CO_2 reforming of methane processes are deactivated very fast due to the sintering of metallic phase and carbon formation (Damyanova et al., 2012). The stability of the catalysts is determined, as seen in Figure 16 and 17. The results show that the Ni/MgAl catalysts posses a more stable performance for 300 min on stream. A decrease of the values of CH_4 and CO_2 conversions with time on stream is detected for Ni/ZrAl. It should be noted that the values of CH_4 and CO_2 conversions slightly increase at the beginning of the reaction up to 60 min. This is because of further catalyst activation.

However, due to the questionable H_2 values obtained in the reaction resulted in presence of high H_2 at the initial stage of the reaction, only the amount of CO produces is to be taken into considerations. Based on this, it is determined that Ni/ZrAl shown as the best catalyst with a higher CO selectivity of 31.3 % in comparison with Ni/MgAl with CO at only 7.6%.

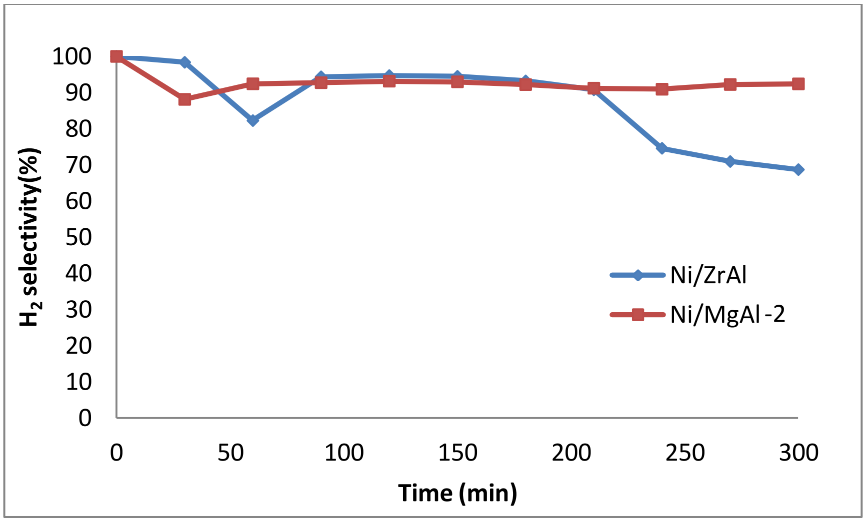


Figure 16: H_2 selectivity (%) on time-on-stream

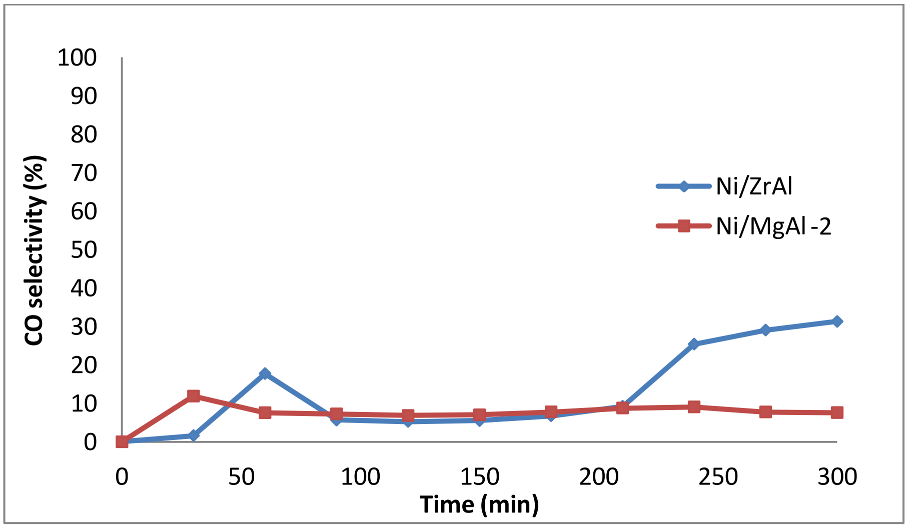


Figure 17: CO selectivity (%) on time-on-stream

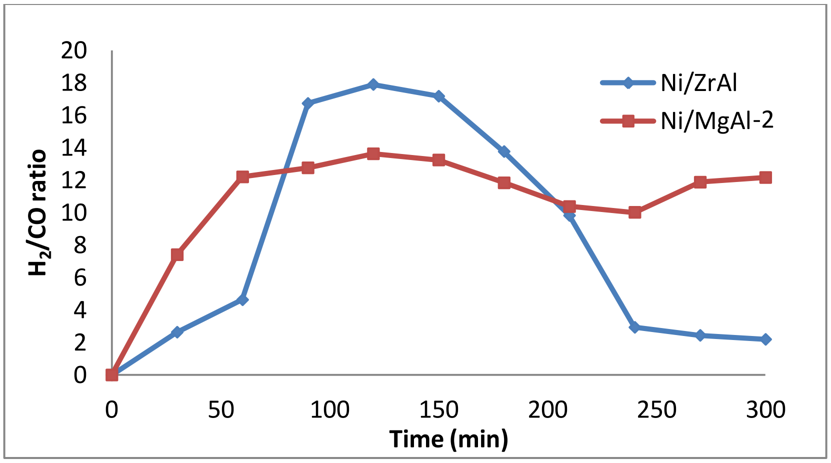


Figure 18: H_2/CO ratio on time-on-stream

It can be concluded that the catalytic performance of Ni-based catalysts supported on various oxides (Al_2O_3, ZrO_2-Al_2O_3, and MgO-Al_2O_3) in the reaction of CO_2 reforming depends strongly on the kind of support. Several conclusions on the catalytic performance can be drawn from the experiment in the reactor:

1) Both catalysts show a good activity towards CO_2 reforming of methane.
2) While a continuous catalyst deactivation is found over Ni-based catalyst supported on both supports, Ni/ZrAl however show to be more effective in CO_2 reforming as it yields more CO than Ni/MgAl-2 although Ni/MgAl-2 exhibits stable performance on stream.
3) The Ni/ ZrAl catalyst also shows a steady and a better H_2/CO ratio throughout the time on stream as the yield for both H_2 and CO is consistent for 300 min on stream.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

4.1 Recommendation

Characterization

Characterization for the catalysts can be done with X-ray photoelectron spectroscopy (XPS) to determine the chemical state of the catalysts. Temperature-programmed Reduction (TPR) analysis can also be done to determine the reducibility and dispersion of Ni particles in the catalysts

H_2 Reduction in Reaction (Blank Run)

More reduction of the amount of H_2 at the initial stage of the reaction should be done. This can be done by adjusting the flow rate of reactant gas, adjusting purging time. Due to time constraint, the blank run for H_2 reduction is done only on one type of catalyst which is Ni/ZrAl. Given that assuming all catalysts would show similar readings of H_2. Therefore, in future work all catalyst should undergo the blank run to get more accurate readings.

Future Works

The analysis of spent catalysts after CO_2 reforming of methane and coke deposition can be determined in more detailed. However, due to time constraints the analysis can only be done to determine the conversion of the reactants and selectivity of products during the reforming reactions

4.2 Conclusion

A significant share of researchers has focused its effort on converting two greenhouse gases into synthesis gas using CO_2 reforming in recent years. This is resulting in synthesis gas being an attractive route in utilizing methane and carbon dioxide in the most efficient way. However, from the literature there are some drawbacks of dry reforming that it is an endothermic reaction which required high reaction temperature to obtain high conversion levels. High reaction temperature results in coke deposition through the dissociation of methane which may cause catalyst deactivation and clogging of the reactor. Therefore it can be concluded that, it is crucial develop an effective catalyst by obtaining optimum performance of the catalyst with respect to CO_2 conversion, product yields and selectivity.

From the characterization study, it can be concluded that all the catalysts show their respective properties similar to the previous works. The effect of ZrO_2 and MgO addition to NI/Al_2O_3 is to improve the activity and stability of the catalyst during CO2 reforming of methane. $Ni/MgO\text{-}Al_2O_3$ catalyst has a good dispersion of active sites and uniform morphology, big crystals of MgO in comparison with the $Ni/ZrO_2\text{-}Al_2O_3$ catalyst. Since the catalyst supported on MgO shows to be a better catalyst in terms of its properties, the difference between various weight percent of MgO present in Ni-based catalyst is also observed. The catalyst with 30% MgO exhibits a larger surface area and a better dispersion of particle compared to the catalyst with 70% MgO. This shows that only moderate addition of the Mg modifier could effectively improve the catalytic properties of the catalysts.

As for the catalytic performance of Ni-based catalysts supported on various oxides (Al_2O_3, $ZrO_2\text{-}Al_2O_3$, and $MgO\text{-}Al_2O_3$) in the reaction of CO_2 reforming, the best catalytic behaviour is showed by $Ni/ZrO_2\text{-}Al_2O_3$. It shows to be more effective in CO_2 reforming as it yields more CO than $Ni/MgO\text{-}Al_2O_3$ although $Ni/MgO\text{-}Al_2O_3$ exhibits stable performance on stream.

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APPENDIX

APPENDIX A: Information on Alumina and Modified Alumina (from SASOL)

APPENDIX B: Materials and Equipments Used

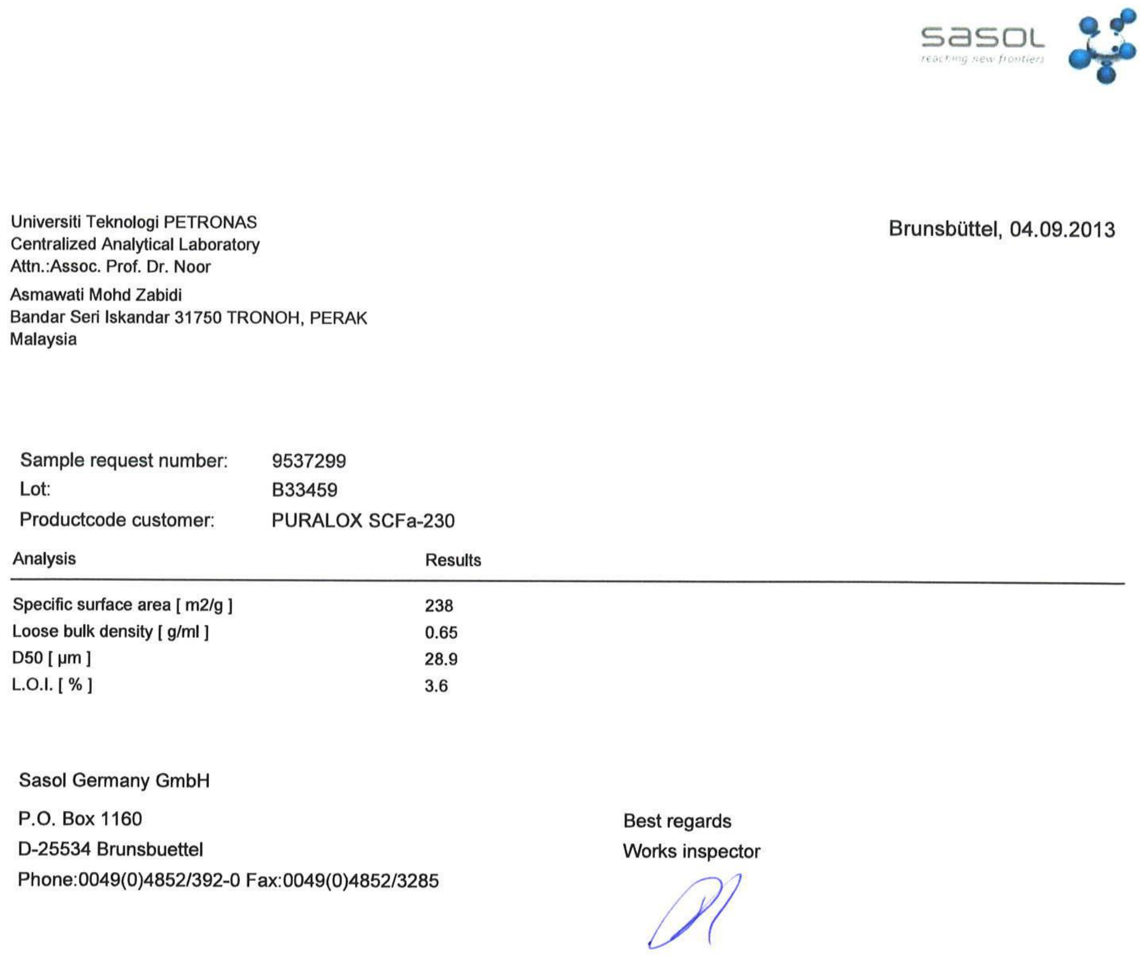
APPENDIX C: Gas Chromatography Valve System

APPENDIX D: Gas Chromatograph

APPENDIX E: Sample Calculations

APPENDIX A

Info on Alumina and Modified Alumina (provided by SASOL)



sasol
reaching new frontiers

Universiti Teknologi PETRONAS
Centralized Analytical Laboratory
Attn.:Assoc. Prof. Dr. Noor
Asmawati Mohd Zabidi
Bandar Seri Iskandar 31750 TRONOH, PERAK
Malaysia

Brunsbüttel, 04.09.2013

Sample request number: 9537299
Lot: B33459
Productcode customer: PURALOX SCFa-230

Analysis	Results
Specific surface area [m2/g]	238
Loose bulk density [g/ml]	0.65
D50 [µm]	28.9
L.O.I. [%]	3.6

Sasol Germany GmbH
P.O. Box 1160
D-25534 Brunsbuettel
Phone:0049(0)4852/392-0 Fax:0049(0)4852/3285

Best regards
Works inspector

Universiti Teknologi PETRONAS
Centralized Analytical Laboratory
Attn.: Assoc. Prof. Dr. Noor
Asmawati Mohd Zabidi
Bandar Seri Iskandar 31750 TRONOH, PERAK
Malaysia

Brunsbüttel, 23.09.2013

Sample request number: 9537328
Lot: BD6601
Productcode customer: PURALOX SBa-200/Zr20

Analysis	Results
Al2O3 (Zr-dop.,100%) [%]	80.4
ZrO2 (Zr-dop, 100%) [%]	19.6
Surface area [m2/g]	211
Loose bulk density [g/ml]	0.66
D50 [µm]	29.4
L.O.I. [%]	1.6

Sample request number: 9537328
Lot: BD4991
Productcode customer: PURALOX Mg 30/180
Developmental Product z500940

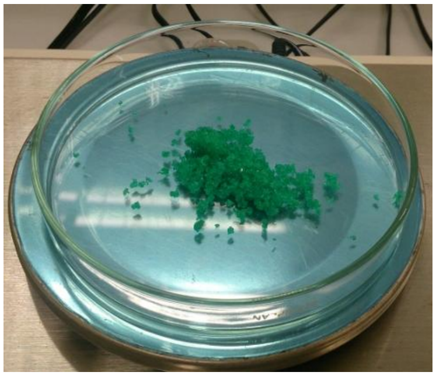
Analysis	Results
AL2O3 (Mg-dop,100%) [%]	71.2
MGO (Mg-dop,100%) [%]	28.8
Surface area [m2/g]	185
Loose bulk density [g/ml]	0.35
D50 [µm]	47.5
L.O.I. [%]	5.4

Sample request number: 9537328
Lot: M7767
Productcode customer: PURALOX Mg 70/110
Developmental Product z500938

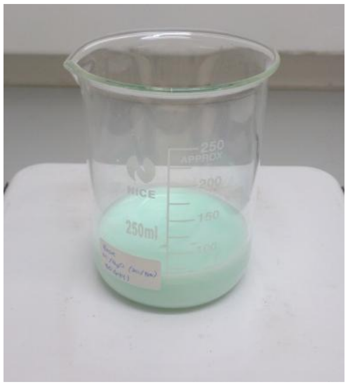
Analysis	Results
AL2O3 (Mg-dop,100%) [%]	30.9
MGO (Mg-dop,100%) [%]	69.1
Surface area [m2/g]	109
Loose bulk density [g/ml]	0.32
L.O.I. [%]	1.7
D50 [µm]	29.2

APPENDIX B

Materials and Equipments Used



Nickel Nitrate



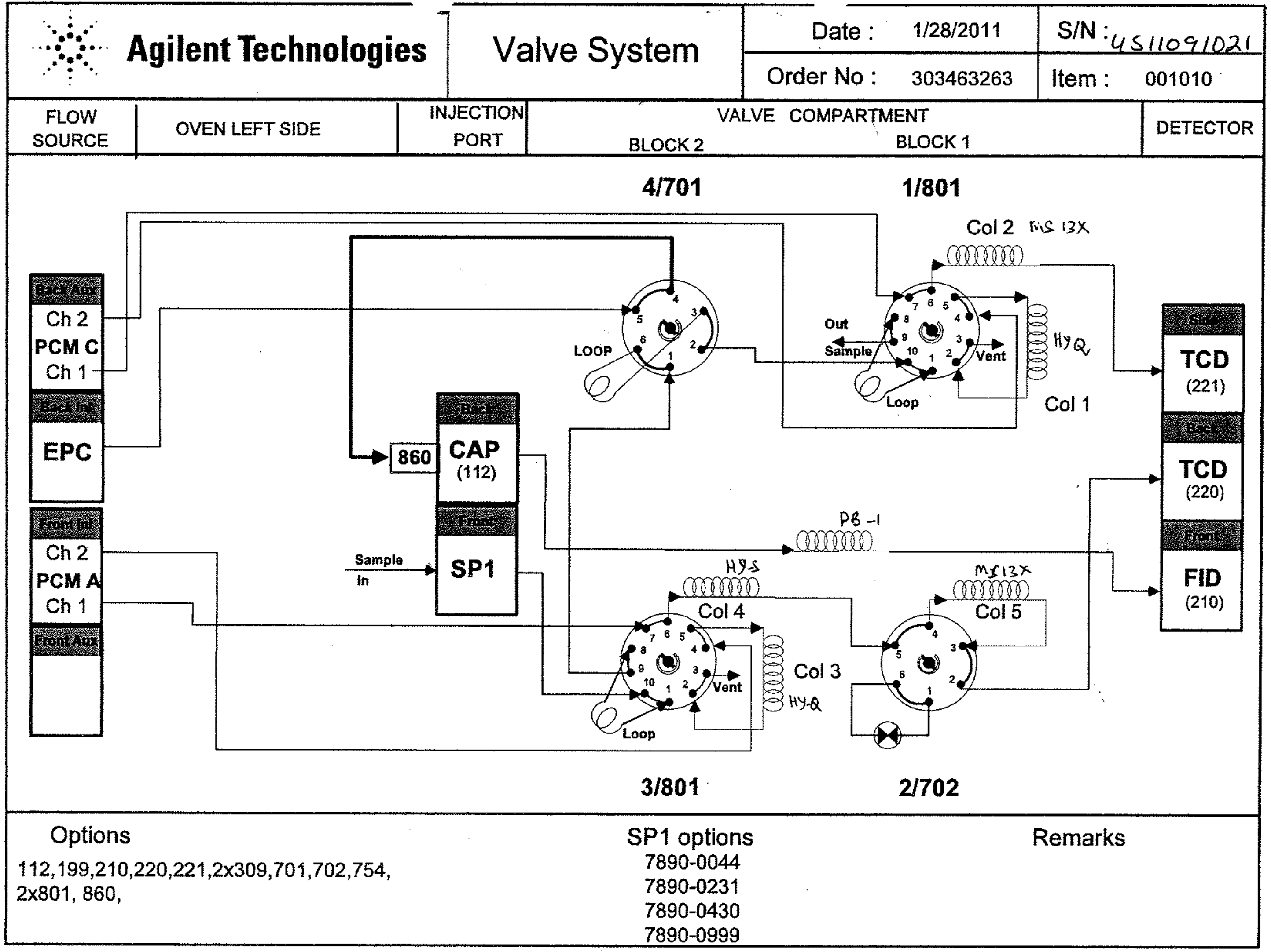
Nickel nitrate solution, $Ni(NO_3)_2.6H_2O$ with various oxides supports

Drying oven used for drying catalyst

Micro-reactor used for the CO_2 reforming reaction

APPENDIX C

GC Valve System



Agilent Technologies Valve System

Date : 1/28/2011 S/N : 4S11091021

Order No : 303463263 Item : 001010

Options

112,199,210,220,221,2x309,701,702,754,
2x801, 860,

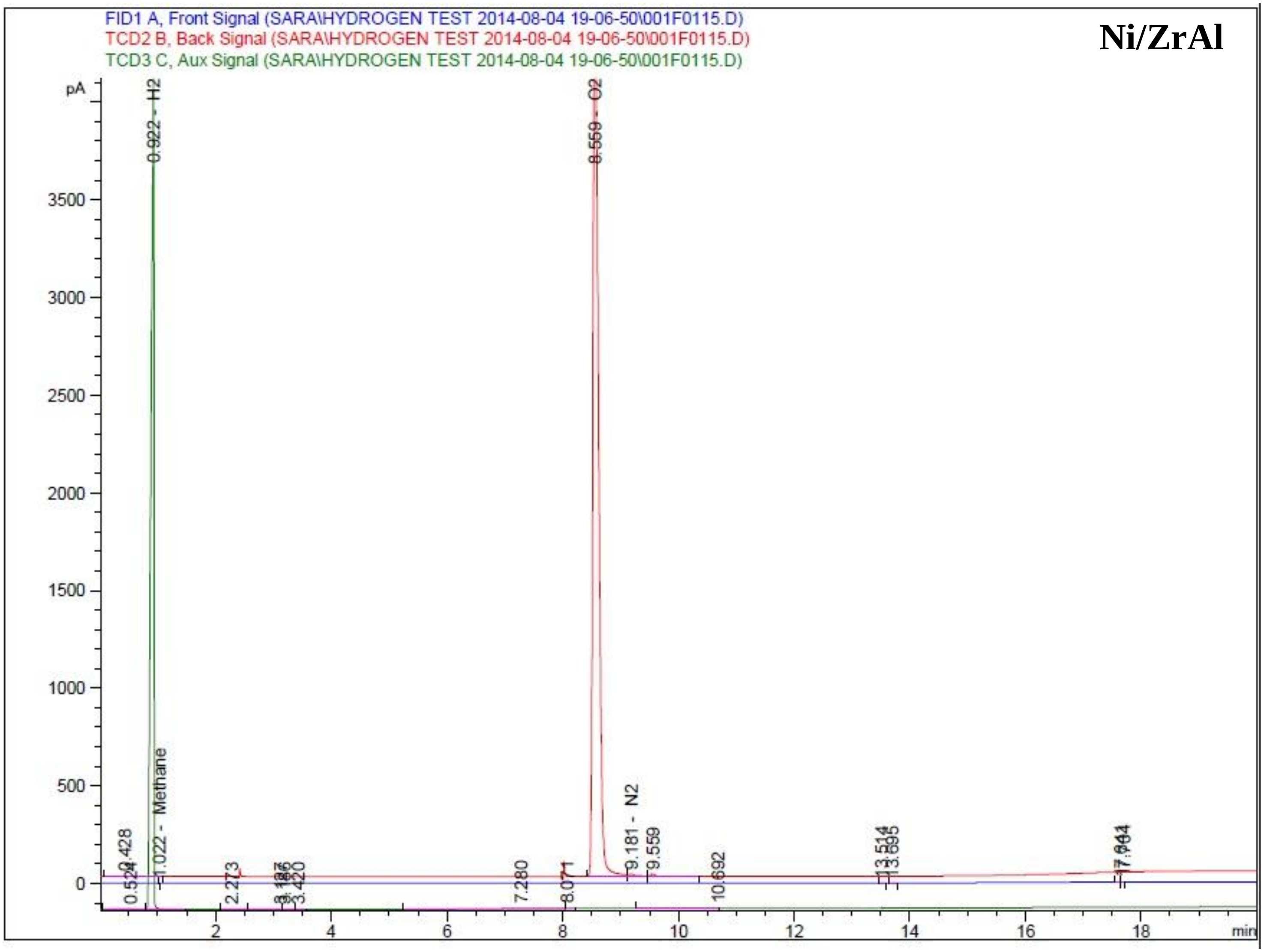
SP1 options

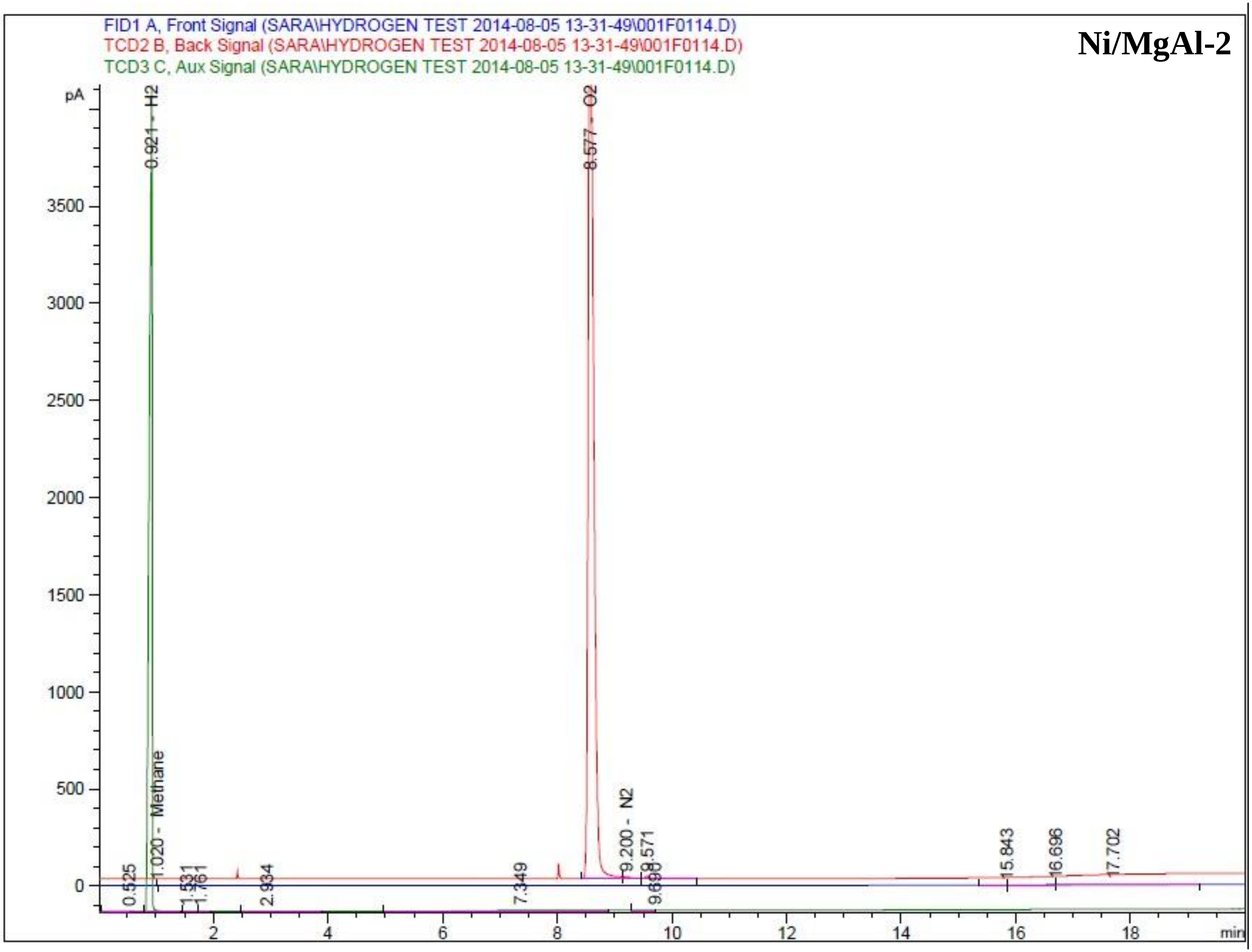
7890-0044
7890-0231
7890-0430
7890-0999

Remarks

APPENDIX D

Gas Chromatograph




Ni/MgAl-2

FID1 A, Front Signal (SARA\HYDROGEN TEST 2014-08-05 13-31-49\001F0114.D)
TCD2 B, Back Signal (SARA\HYDROGEN TEST 2014-08-05 13-31-49\001F0114.D)
TCD3 C, Aux Signal (SARA\HYDROGEN TEST 2014-08-05 13-31-49\001F0114.D)
pA
3500
3000
2500
2000
1500
1000
500
0
0.921 - H2
8.577 - O2
1.020 - Methane
9.200 - N2
0.525
1.531
1.761
2.934
7.349
9.571
9.690
15.843
16.696
17.702
2
4
6
8
10
12
14
16
18
min

APPENDIX E

Sample Calculations

Standard Solution

The standard solution is then mixed with the supports. Sample calculation was done in preparing the standard solution:

0.2 g/ml of Ni,
MW of $(NO_3)_2$ = 182.32 g/mol
MW of Ni = 58.69 g/mol
For 250 ml of solution; need 50 g of Ni

Therefore, amount of $(NO_3)_2$ needed = (50 g of Ni / 58.69) × 182.7032 mol $Ni(NO_3)_2$
= 155.6420 g of $Ni(NO_3)_2$

CH_4 and CO_2 Conversion

Conversions describe as ratios how much of a reactant has reacted (X — conversion, normally between zero and one). For the conversions of the reactant feed, data taken at 300 min:

Blank = 1031.66

time (min)	CO_2	CH_4	CO	H_2	H2 - blank
0	39.97	83.96	0	236.05	236.05
300	28.41	73.24	12.56	1004.1	27.56

$$X_{CH_4}\ \% = \frac{C_{CH_{4,in}} - C_{CH_{4,out}}}{C_{CH_{4,in}}} \times 100$$

$$X_{CH_4}\ \% = \frac{83.96 - 73.24}{83.96} \times 100 \quad = 12.77\%$$

$$X_{CO_2}\,\% = \frac{C_{CO_{2,in}} - C_{CO_{2,out}}}{C_{CO_{2,in}}} \times 100$$

$$X_{CO_2}\,\% = \frac{39.97-28.41}{39.97} \times 100$$ = 28.92%

H_2 and CO Selectivity

Selectivity described as how much of a desired product was formed (Y — yield, normally also between zero and one) and how much desired product was formed in ratio to the undesired product.

$$Y_{H_2}\,\% = \frac{C_{H_{2,net}} - C_{H_{2,blank}}}{\left(C_{H_{2,net}} - C_{H_{2,blank}}\right) + C_{CO}} \times 100$$

$$Y_{H_2}\,\% = \frac{27.56}{27.56+12.56} \times 100$$ = 68.94%

$$Y_{CO}\% = \frac{C_{CO}}{\left(C_{H_{2,net}} - C_{H_{2,blank}}\right) + C_{CO}} \times 100$$

$$Y_{CO}\% = \frac{12.56}{27.56+12.56} \times 100$$ = 31.31%