Ethylene Production from Bioethanol Dehydration over Bimetallic Alkaline Earth Oxide-Alumina Catalyst

by

SIM SIANG LENG

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University Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

ETHYLENE PRODUCTION FROM BIOETHANOL DEHYDRATION OVER BIMETALLIC ALKALINE EARTH OXIDE-ALUMINA CATALYST

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A project dissertation submitted to the
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Approved by,

Main Supervisor
(Dr. Bawadi Abdullah)

Approved by,

Co-Supervisor
(AP. Dr. Suzana Yusup)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
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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.

(SIM SIANG LENG)

ABSTRACT

This research will be focusing on preliminary development studies on catalyst that can help increase the resistance of catalyst toward coke formation which mainly due to decomposition of carbon.

Research found that alkaline earth metal oxide has the basic property that might be able to help increase catalyst's resistance toward coke formation during the catalytic bioethanol dehydration process. In the research, two kinds of alkaline earth oxide metals are impregnated with nickel on the alumina, which are magnesium oxide and calcium oxide. A preliminary characterization on the catalysts been carried out with Sieve Shaker, FTIR, FESEM, EDX, and TGA. The prepared catalysts have been tested with catalytic dehydration process to find out its effectiveness in converting ethanol to ethylene and the spent catalysts were tested on total carbon content analysis using CHNS. Results show that CAT5 is the most effective catalyst with ethylene conversion of 65.36% and total carbon content or 1.323wt%.

ACKNOWLEDGMENTS

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INTRODUCTION

1. INTRODUCTION

1.1 Background of Study

The increasing demand of ethylene is due to its uses in producing polyethylene, one of the primary components in most of the plastic; and in petrochemical industry. Thus, it is essential to increase the production of ethylene in chemical industry and making it economically valuable. In year 2011, there are total of 141million tonnes of ethylene been produced in global (Warren R,2012). Initially, ethylene is mainly produced from steam-cracking of petroleum or natural gas feedstock. Later, alternative method has been developed which is catalytic dehydration of ethanol to ethylene. However, due to the high production cost and energy consumption, this method was not widely used in many countries. Nowadays, due to the depletion of natural resources and energy, skyrocketing of crude oil price, and most important is the development of bioethanol which can be obtained from renewable sources, namely, biomass and sugars through enzymatic processes, catalytic dehydration of bioethanol has once again brought up to the production line and getting much more attention.

In dehydration of bioethanol to produce ethylene, catalyst is used to increase the rate of selectivity of the chemical reaction and reduce the activation energy of the process without being consumed at the end of the reaction. Bimetallic catalyst is an advance type of catalyst which produced by combining two types of metal. There were some researches been done and proven that bimetallic catalyst is able to further improve the selectivity of a reaction by comparing with its individual parent metals (H. Idriss et al, 1992; F.Epron et al, 2001; W.L.Gao et al, 2004; F.B. Noronha et al, 1997; R.Melendrez et al, 2000). Thus, bimetallic catalyst will be used in this research for bioethanol dehydration to form ethylene. However, coke formation on the catalysts mostly due to decomposition of ethylene will cause the deactivation of catalyst. This will decrease the lifespan of catalyst. Therefore, improving the resistance of catalyst toward coke formation is essential in order to extend the lifespan of catalyst at the same time reducing the cost of regenerating and turn over to change the catalyst which consumes a lot of cost. It was reported that addition of basic metal oxide into the catalyst can help to reduce the formation of coke on the surface of catalyst (K.Y.Koo et al, 2008). In this research, alkaline earth metal oxide which is one of the important basic metal oxides will be added to the catalyst to test its effectiveness in reducing the formation of coke on catalyst's surface. Some of the alkaline earth metals are magnesium (Mg), calcium (Ca), strontium (Sr), and barium (Ba). The focus of this research will be on two alkaline earth oxide which are magnesium oxide (MgO) and calcium oxide (CaO) due to time constraint.

For this experiment study, bimetallic alkaline earth oxide-alumina catalyst needed to be prepared and characterized before proceeding to test the effectiveness of reducing coke formation on the surface of catalyst in ethylene production process using hydrocracker rig. Further study on the spent catalysts will be carried out after the process to study the coke formation on catalysts after the reactions.

1.2 Problem Statement

Production of ethylene from bioethanol dehydration using the current available catalyst such as $TiO_2/\gamma\text{-}Al_2O_3$(Chen,G et al, 2007), $Ag_3PW_{12}O_{40}$(Gurgul, J et al, 2011), alumina, nano-HZSM5 zeolite(Bi, J. et al, 2010) and so on, although is able to produce high conversion and selectivity of ethylene production, the decomposition of ethylene to cause the formation of coke at the surface of catalyst is still occurring which reduced the lifespan of the catalyst in the catalytic dehydration process. In order to increase the lifespan of catalyst and reduce the regeneration or turnover rate of the catalyst especially in mass production industry which can help save up a lot of cost, a better catalyst need to be prepared. In this research, the focus is on making a bimetallic catalyst with alkaline earth metal which possesses basic property that can help prevent the formation of coke on the surface of catalyst. Characterization of catalyst is needed after the catalyst been prepared as well as after the reaction to identify the optimum catalyst that able to reduce coke formation during catalytic dehydration process at the same time maintaining the production rate.

1.3 Objectives

The objectives that need to be achieved throughout the research process are:

(a) To synthesize bimetallic catalyst using alkaline earth metals.
(b) To do preliminary characterization on the prepared catalyst.
(c) To test the effectiveness of prepared catalyst in converting ethanol to ethylene in the catalytic dehydration process using fixed-bed micro-reactor (hydrocracker rig).
(d) To characterize and synthesize the spent catalyst in order to study the coke formation on the surface of catalyst after reaction.

1.4 Scope of Study

Throughout the research, student will be exposed to:

1. Literature review related to the research project
2. Prepare catalyst with different alkaline earth oxide and different composition
3. Characterized the catalyst using Sieve Shaker, FTIR, TGA, FESEM and EDX.
4. Produce ethylene using the prepared catalyst via catalytic bioethanol dehydration process.
5. Study the coke formation of the spent catalysts using FESEM and CHNS.
6. Evaluate each types of catalyst based on the amount of carbon deposited on the surface of catalysts to find out the most suitable catalyst in reducing coke formation on catalytic bioethanol dehydration process.

1.5 Relevancy of the Project

This research will be focusing on reducing the coke formation on catalyst that used for bioethanol dehydration process in producing ethylene. This will help to reduce the cost of operation in producing ethylene from bioethanol at the same time convince the ethylene production plant to use bioethanol dehydration as the primary production route. If the implementation of newly developed catalyst is able to reduce the cost of changing and renewing catalyst until it’s lower than the commercial method which is production of ethylene through steam cracking of petroleum and natural gas, then ethylene production plant will slowly moving their production method to bioethanol catalytic dehydration. Indirectly this will help to prevent the depletion of natural resources and prevent the release of greenhouse gases through steam cracking process which are the main concern in the society.

1.6 Feasibility of Project

This project is given to the student with condition of completing it within eight months. This time frame can be divided into two sections. The first half of the project will be mainly focus in literature review, understanding the basic concept and principle of the project. After that, planning on the experiment procedure will be carried out to have an idea on the way to set up the experiment before proceeding to the real experiment. Last but not least, sample preparation and some part of the catalyst preparation can be done in the first half of the research. The catalyst preparation will be continued on the second part of the project followed by characterization of catalysts using analyzing tools. Due to unavailability and limited slot given for each student to analyze their samples, the characterization part of the research has been simplified to preliminary analysis whereby not all the samples will be sent for characterization. This is to ensure student is able to complete the objectives within the short time frame given. Testing the catalysts’ effectiveness in bioethanol dehydration process was carried out along with the characterization process. The last part of this research will be to study the coke formation on spent catalysts after the process and decide on which catalyst is most effective in increasing coke formation resistance. The project is feasible within the time frame given with proper planning.

The apparatus the chemicals needed for catalyst preparation is easily available and orderable inside the University. Besides, the main equipment needed for the process which is the hydrocracker rig for bioethanol dehydration is also located in the research lab of UTP. This will ease the student in carrying out all the research inside UTP. Therefore, structural and organize planning on the experiment is very important in order for the student to complete the research within the time frame given.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 Ethylene

Ethylene is one of the hydrocarbon compounds with a chemical formula of C_2H_4. It is in massive production in petrochemical industries. In year 2011, a total of 141million tonnes of ethylene been produced in global (Warren R, 2012). Top ethylene production complexes were listed in Table 1.

Table 1: Top industrial ethylene complexes and their locations ranked by capacity (Warren R, 2012)

Company	Location	Megaton/year
Steam-cracking plants	-	-
Formosa Petrochemical Corporation	Mailiao, Taiwan	2.94
Nova Chemicals Corporation	Joffre, Alberta, Canada	2.81
Arabian Petrochemical Company	Jubail, Saudi Arabia	2.25
ExxonMobil Chemical Company	Baytown, TX, USA	2.20
ChevronPhillips Chemical Company	Sweeny, TX, USA	1.87
Dow Chemical Company	Terneuzan, Netherlands	1.80
Ineos Olefins & Polymers	Chocolate Bayou, TX, USA	1.75
Equistar Chemicals LP	Channelview, TX, USA	1.75
Yanbu Petrochemical Company	Yanbu, Saudi Arabia	1.71
Equate Petrochemical Company	Shuaiba, Kuwait	1.65
Ethanol to ethylene plants	-	-
Braskem	Triunfo, Brazil	0.20
Dow Chemical Company	Santa Vitoria, Brazil	0.19
Solvay Indupa	Santo Andre, Brazil	0.06

Ethylene is one of the most consumed intermediate product use in chemical industries. One of the major uses is in the production of polyvinyl chloride (PVC). PVC is widely needed for making plastics, pipe, doors, fencing and etc. There are two methods to produced ethylene which are by steam cracking of hydrocarbon and catalytic dehydration of ethanol. Till todays, steam cracking of hydrocarbon is still dominating the production market due to the high production cost and energy consumption of catalytic dehydration method. However, with the increase of crude oil price and shortage non-renewable natural resource and energy, catalytic dehydration of ethanol to produce ethylene is getting a lot of attention. Furthermore, introduction of bioethanol which can be produced by fermentation of biomass which is consider as a renewable source making the catalytic dehydration method to become more and more competitive.

2.2 Bioethanol Catalytic Dehydration

There are two reactions occur at the same time in bioethanol catalytic dehydration to produce ethylene which can be shown in *Equation 1 and 2*.

$$C_2H_5OH = C_2H_4 + H_2O \qquad +44.9\ kJ/mol \qquad (1)$$

$$2C_2H_5OH = C_2H_5OC_2H_5 + H_2O \qquad -25.1\ kJ/mol \qquad (2)$$

Equation 1 is the main reaction with desired product as ethylene. In the reaction, the acid catalyst first protonates the hydroxyl group and make it leave as water molecule leaving the positive charge methyl which later deprotonated by the conjugate base of catalyst forming ethylene after rearrangement of hydrocarbon. The reaction mechanism is shown in *Figure 1*.

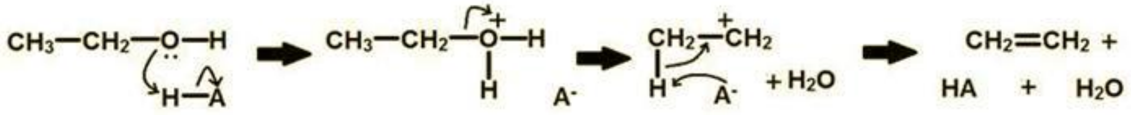


Figure 1: Reaction mechanism for dehydration of ethanol to ethylene.

Equation 2 is the side reaction of ethanol dehydration which forms the undesired product. From the heat of reaction given, the main reaction is endothermic while the side reaction is exothermic. Therefore, in order to increase the selectivity and conversion of reaction forming desired product, high reaction temperature is required. The reaction temperature range is from 180°C to 500°C (D.Fan et al, 2013).

Many researchers have seen the great potential in developing catalytic dehydration process to produce ethylene from bioethanol. So far, there are many researches been done in finding the best catalyst to dehydrate ethanol in term of conversion, selectivity, reaction temperature, and lifespan of catalyst which can be summarized in *Table 2*.

Table 2: Summary of catalysts for the bioethanol dehydration process and their catalytic ability

Catalyst	Max ethylene selectivity	Ethanol conversion	Reaction temperature	Hourly space velocity	Lifespan	Ref
TiO_2/γ-Al_2O_3	99.4%	99.96%	300-500 °C	26-234 h^{-1}	400h	(Chen, G.W et al, 2007
HZSM-5	98.5%	97.3%	300 °C	-	60h	(Zhang, et al., 2008)
Fe_2O_3	65.4%	96.96%	500 °C	2.85 h^{-1}	-	(Zaki, T., 2005)
Mn_2O_3	58%	90.10%	500 °C	2.85 h^{-1}	-	(Zaki, T., 2005)
Al_2O_3	91.9%	90.10%	475 °C	-	80h	(Zhang, et al., 2008)
NiAPSO-34	98.3%	96.5%	375 °C	-	>100h	(Zhang, et al., 2008)
SAPO-34	94.3%	93.5%	375 °C	-	>100h	(Zhang, et al., 2008)

From *Table 2*, it clearly shown that most of the catalyst developed can achieve a very high ethanol conversion to form ethylene which is >90%. However, the lifespan of the catalysts are very short, which required frequent changing of catalyst that will cost a lot of money. The short lifespan of catalyst is mostly due to the deposition of coke formation on the active sites of catalyst caused the deactivation of catalyst. Therefore, this research will be focused on developing a catalyst that is able to increase the resistance of catalyst toward coke formation, at the same time maintaining the acceptable conversion rate.

2.3 Coke formation on catalyst (Deactivation of catalyst)

Coke formation is a type of physical fouling whereby the surface is covered with deposited carbon. During coke formation on catalyst, carbonaceous residues will form and cover the active surface sites of the catalyst which can be illustrated in *Figure 2*.

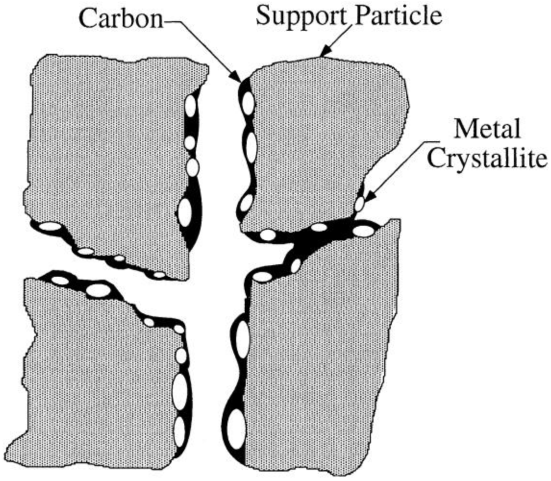


Figure 2: Conceptual model of fouling, crystallite encapsulation and pore plugging of a supported metal catalyst due to carbon deposition (H.B. Calvin, 2001).

When a layer or might be multilayers of chemisorbed carbon formed on the surface of catalyst active surface sites, it will block access the reactants to attach with the catalyst. It might also totally encapsulate the metal particle of catalyst thus, completely deactivate the catalyst. For the worst, the strong carbon filaments that build-up in pores may stress and fracture the support material on catalyst caused disintegration of catalyst(H.B. Calvin, 2001).The decrease of active surface area will slowly deactivating the catalyst and cause decrease in the yield of product. For catalytic dehydration of bioethanol forming ethylene, the main cause of coke formation is due to the decomposition of ethylene forming carbon compound as shown in *Equations 3 and 4.*

$$C_2H_4 = 2C + 2H_2 \qquad (3)$$

$$C_2H_4 = C + CH_4 \qquad (4)$$

These are the two kind of reaction that possibly occurs in decomposition of ethylene. There are report shows that catalyst precoated with MgO and CaO showed high activity in methane-to-syngas conversion as compared to the catalyst without precoating(V.R. Choudhary et al, 1995). In another research study, the effect of MgO on coke formation over MgO-promoted Ni/Al_2O_3 has been investigated (K.Y.Koo, 2008). It was found that addition of MgO improves the dispersion of Ni particles, resulting in the strong interaction with support; thus the highly dispersed Ni particles are hard to oxidize. The optimum content of MgO for suppressing coke formation is 20wt%. These proven that the alkaline earth metals have the basic property that can help reduce the formation of coke on the catalyst. However, there was research showed that Ni/Al_2O_3 impregnated with 5wt% of CaO tested in ethanol steam reforming has the ability to reduce the dehydration of ethanol and thus reduce polymerization of ethylene forming coke (Elias, Lucrédio, & Assaf, 2013). Therefore, for this research the weight percent of alkaline earth oxides were maintain below 5wt% in order to maintain the production rate of ethylene at the same time reduce coke formation. The aim of this research would be to study two kinds of alkaline earth oxide metals which are MgO and CaO with different composition in reducing coke formation in bioethanol dehydration process.

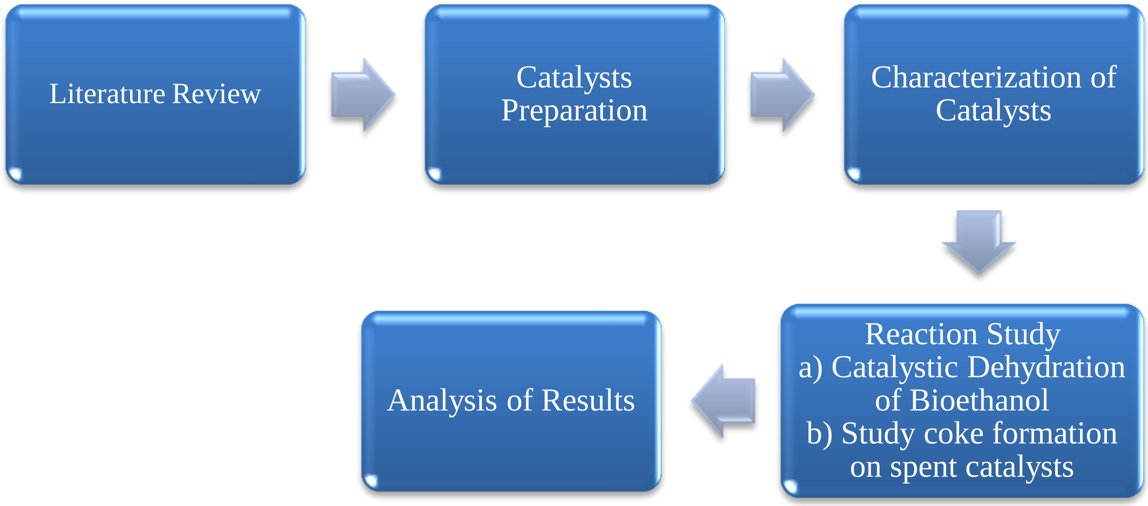
CHAPTER 3

METHODOLOGY/PROJECT WORK

3. METHODOLOGY/PROJECT WORK

3.1 Methodology

The methodology explains in brief the activities that been carried out throughout this research work which is illustrated in the flow diagram below:



This project is mainly experimental based research whereby different types and composition of catalysts need to prepare at the beginning stage of experiment after a thorough literature review has been done. A basis catalyst will be prepared to compare with the new developed catalysts. Followed by characterization of prepared catalysts to find out the surface area, porosity, structure, and other properties of the catalysts and compared with the basis catalyst. After that, reaction study can be carried out for bioethanol dehydration to ethylene using the prepared catalyst. After the reaction, the structure and properties of the used catalyst is further investigated to study the coke formation on it. Analysis of results will be carried out after all the experimental works have been done to find out the catalyst with optimum resistance toward coke formation during bioethanol dehydration process. Throughout the experimental process, continuous reviewing literature will be needed in finding solution or explanation on the conditions and results obtained.

3.2 Chemicals and Equipment

3.2.1 Chemicals

Throughout the experimental works, all the chemicals needed are listed below:-

a) Ethanol (95% purity)
b) Nickel Nitrate, $Ni(NO_3)_2.6H_2O$
c) Methanol
d) Gamma Aluminium Oxide, γ-Al_2O_3
e) Magnesium Nitrate, $Mg(NO_3)_2$
f) Calcium Nitrate, $Ca(NO_3)_2$

3.2.2 Equipment

There are two kinds of instruments that will be widely used in this research, which are analytical instruments and experimental instrument. Analytical instruments will be used in characterization of catalysts which are listed below with its functionality:-

a) Fourier Transform Infrared (FTIR) – To determine the surface concentrations of active intermediates

b) Field Emission Scanning Electron Microscopy (FESEM) – To study surface structure of the catalysts before and after reaction
c) Energy Dispersive X-ray (EDX) – To determine the components present in the catalysts
d) Thermogravimetric Analysis (TGA) – To study the decomposition rate of the catalysts.
e) Total Carbon Content or CHNS – Study the amount of carbon present on the spent catalysts

The experimental instruments needed in this research branched into two categories which are for catalyst preparation and catalyst testing. Below shows the instruments needed for catalyst preparation:-

(a) Sieve Trays

The size of sieve trays that used in this experiment is 45µm and 125µm as shown in *Figure 3*. The sieve trays are used to size the alumina that will be used as support in preparing catalyst. The sizing of alumina is very important to ensure that the catalysts are produced from a standard range of size of support and improve consistency of the results obtained.

(b) Sieve Shaker

It is used to shake the sieve trays containing sample with certain amplitude and time to allow the sample to be sieved into different sizes. The model of sieve shaker is *Retsch AS 200 digit* as shown in *Figure 3*.

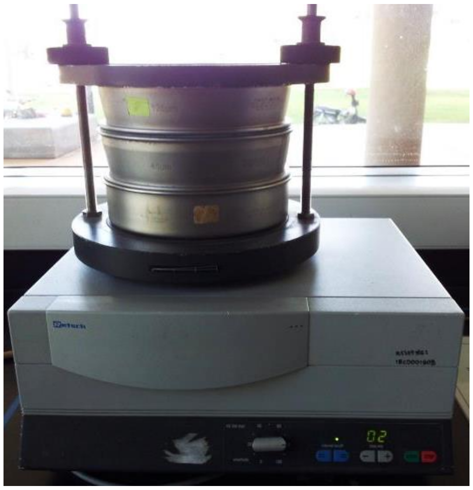


Figure 3: Sieve Shaker with Sieve Trays (45µm & 125µm)

(c) Weighing Balance

It is used to weigh the sample or chemicals need for the experiment. The weighing balance used is from *AND Company Limited*.

Figure 4: Weighing Balance

(d) Hotplate Stirrer

While mixing the alkaline earth oxide solution with the support of catalyst, hotplate stirrer with magnetic stirrer bar is needed to ensure thorough stirring and mixing of solutions. The hotplate stirrer available in the lab is *Thermo scientific super-nuova* hotplate stirrer.

Figure 5: Hotplate Stirrer

(e) Furnace Chamber

The furnace chamber is used to calcine the catalyst. In the laboratory, *WiseTherm Chamber Furnace* is used.

Figure 6: Furnace Chamber

For testing the catalyst produced on bioethanol dehydration process, there are two main equipment required which are:-

(a) Hydrocracker Experimental Rig. Figure 7 shows the schematic diagram of hydrocracker rig.

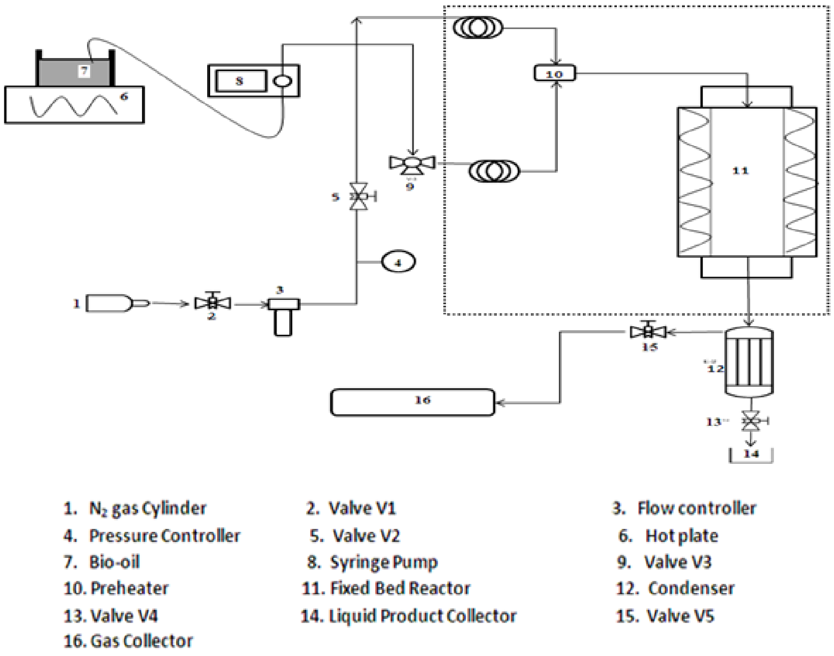


Figure 7: Schematic Diagram of Hydrocracker Experimental Rig

(b) Gas Chromatography-Mass Spectrometry (GC-MS). This equipment is used to identify the amount of ethylene produced from the reaction.

3.3 Project Activities

3.3.1 Literature Review

Thorough readings have been done at the beginning of the research in order to understand the concept and gain information on the research, at the same time, generating ideas in carrying out the experimental works. After starting the experiment, reviewing articles and journals from time to time will be needed to find explanation on the occurrence of certain situation in the process as well as to find explanation on the results obtained by comparing with other researches.

3.3.2 Support Preparation

The support of catalyst which in this experiment is aluminum oxide (γ-alumina) is pre-calcined in air using furnace chamber at 900^{o}C for 12 hours with an increment of temperature at 5^{o}C/min.

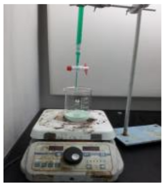
3.3.3 Standard Solution Preparation

Standard solution of 2g/ml of $Ni(NO_3)_2$, $Mg(NO_3)_2$, and $Ca(NO_3)_2$ are prepared by mixing the correct amount of these chemicals in powder form with deionized water as shown in *Figure 8*.

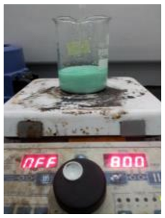
Figure 8: Prepared standard solution for $Ni(NO_3)_2$ and $Mg(NO_3)_2$

3.3.4 Catalyst Preparation

The catalysts that prepared are bimetallic alkaline earth oxide-alumina catalysts. In this research, two different kinds of catalysts are prepared using different alkaline earth oxide metals which are $Ni\text{-}MgO/Al_2O_3$ and $Ni\text{-}CaO/Al_2O_3$. For each kind of catalyst, the wt% of Ni is fixed at 10wt% while varying the composition of alkaline earth oxide at 2wt% and 4wt%. A basis catalyst, Al_2O_3 will be prepared in order to compare with the newly developed catalysts. The catalysts are prepared by using impregnation method. The proper procedure for preparing the catalyst is listed step-by-step as shown below:-



$Mg(NO_3)_2$ solution followed by $Ni(NO_3)_2$ solution are added on the powdered γ-Al_2O_3 using pipette. Ensure the solution is distributed evenly on the surface of the alumina.



30ml of deionized water is added to the solution and stirs the solution for 1h with magnetic stirrer bar at 800rpm at room temperature. (Deionized water is used to facilitate the stirring process)

Dry the solution after 1h in oven at 100^{o}C for overnight. Calcine the catalyst at 500^{o}C for 6h with heating rate of 5^{o}C/min. The high reaction temperature will ensure thermal stability treatment.

Store the catalyst in glass bottle and keep in cabinet for further analysis.

There are five (5) different catalysts been prepared with two different alkaline earth oxide metals impregnated on it with different composition as shown in *Table 3*.

Table 3: Composition of prepared catalysts

Sample Name	Compositions (wt%)			
	Ni	MgO	CaO	Al_2O_3
CAT 1	-	-	-	100
CAT 2	10	2	-	88
CAT 3	10	4	-	86
CAT 4	10	-	2	88
CAT 5	10	-	4	86

3.3.5 Preliminary Characterization of Catalysts

The prepared catalysts have been characterized using Sieve Shaker, FTIR, TGA, FESEM and EDX to identify the structure and properties of the catalysts and compare with the basis catalyst.

3.3.6 Catalytic Reaction

The prepared catalysts and the basis catalyst have been tested on ethylene production by bioethanol dehydration. The operating condition of the reaction is presented in Table 4.

Table 4: Operating condition of Catalytic Dehydration of Ethanol

Pre-heat Temperature	200^oC
Reaction Temperature	450^oC
Pressure	1bar
Flow Rate of Ethanol	1ml/min
Flow Rate of N_2	50ml/min

The actual hydrocracker rig in the laboratory in presented in *Figure 9.*

Figure 9 : Actual Hydrocracker Rig

Procedures for running the catalytic dehydration process using hydrocracker rig are listed below:

1. Switch on the main switch of the equipment, HPLC pump and air compressor.
2. Switch on the attached PC and its software (HYDRO)
3. Take out the fixed bed reactor and clean it with water, after that dry it with air compressor gun.
4. Install back the fixed bed reactor and clean it by flowing in methanol (5ml/min) with nitrogen gas (100ml/min) until the methanol at the outlet of the condenser is clean.
5. Take out the fixed bed reactor, clean it with water and dry it with air compressor gun.
6. Put 2g of catalyst in the fixed bed tube with glass wool in between.
7. Install back the fixed bed tube to the reactor and tighten it.
8. Switch on the Heater, Chiller, Reactor Temperature Controller and Reactor Pressure Controller.
9. Set the pre-heat temperature and reactor temperature at 200^{o}C and 450^{o}C respectively.
10. Open the valve for N_2 and set the flow rate to 50ml/min using the software in the PC.
11. Purge the whole system for 1min using vacuum pump before starting the reaction.
12. Ensure the temperature has reached the desired temperature. Set the ramping rate and flow rate of HPLC pump at 1ml/min and press RUN to start the experiment for 2 hours. (Ensure there are no bubbles in the tube by sucking up the bubbles using syringe.)
13. Connect the gas bag to the gas collecting tank to collect the gas.
14. After the reaction, turn off the heater and set the flow rate of N_2 and ethanol to 0ml/min. Wait till the reactor temperature reach below 300^{o}C then collect the liquid sample.
15. The collected liquid sample is filtered before storing in vial for further analysis.
16. After cooling down the reactor temperature to below 50^{o}C, take out the fixed bed reactor and collect the spent catalyst.

17. Clean the fixed bed tube and start again the procedures from step 1 to continue for the next catalyst.

3.3.7 Study the Production of Ethylene

The sampling of the product after catalytic dehydration is occurred in two forms which are liquid and gas. The liquid product is filtered and stored in vial while the gas product is stored in gas bag as shown in *Figure 10*. Both were sent for GC-MS analysis to identify the content of ethylene. Due to unavailability of standard ethylene, the actual concentration of ethylene in the product could not be identified. Therefore, the amount of ethylene presence in the product was estimated based on the area under the ethylene peak identified by GC-MS in the chromatogram.

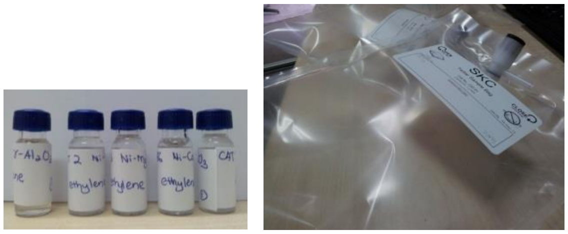


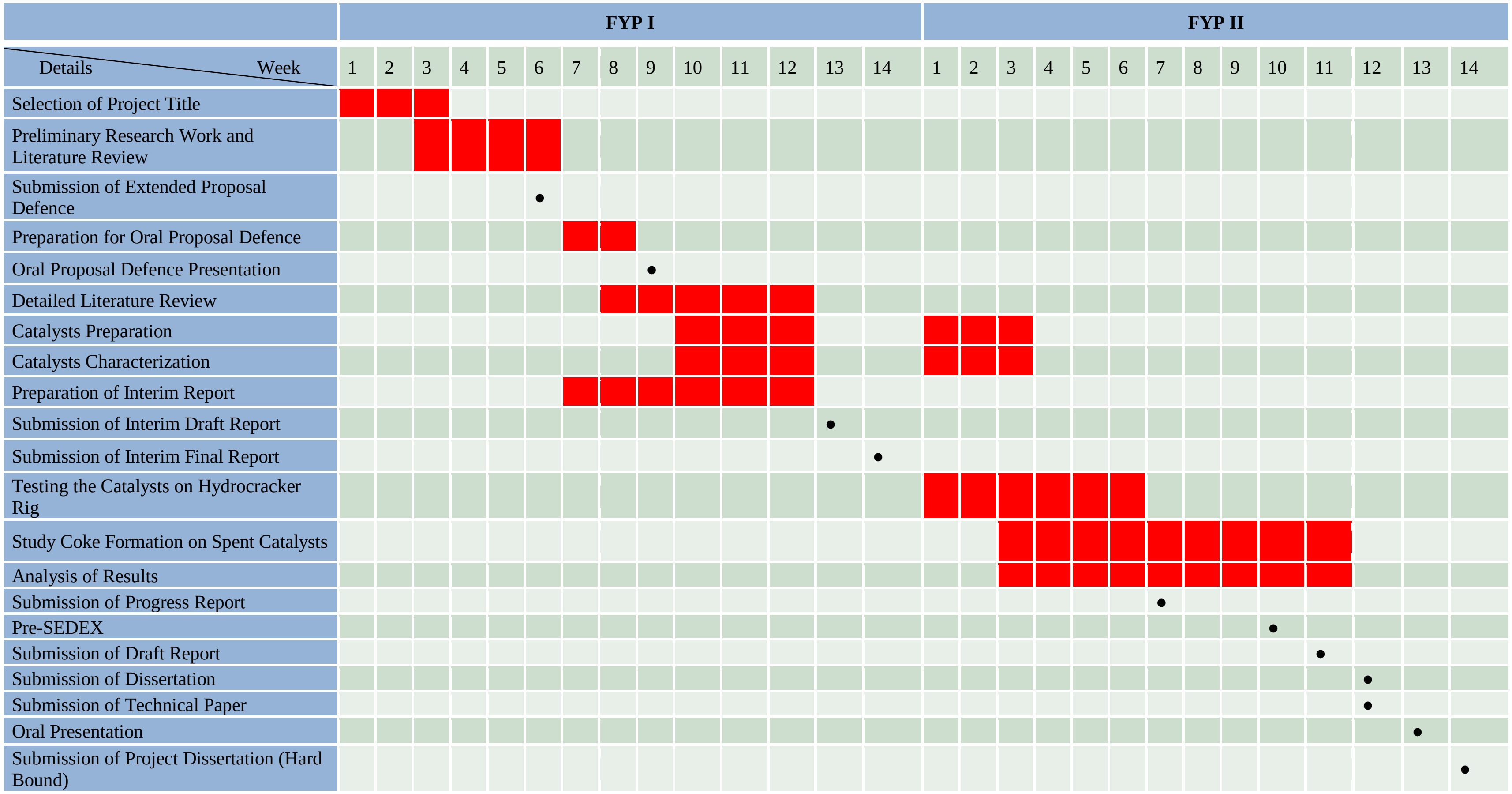
Figure 10: Sampling of products (left: liquid; right: gas)

3.3.8 Study Coke Formation

After the reaction, the spent catalysts are collected as shown in *Figure 11* and the amount of coke formation on the surface of the spent catalysts are studied using FESEM and CHNS. The results are compared with the basis catalysts to find out the effectiveness of new developed catalysts in improving the resistance of coke formation on catalyst after the bioethanol dehydration process. Due to limitation of sample allow to be sent for FESEM analysis, there are only one catalyst had been chosen to send for analysis based on result of total carbon content analysis using CHNS.

Figure 11: Spent catalysts collected

3.4 Gantt Chart and Key Milestone



	FYP I														FYP II													
Details / Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Selection of Project Title	🟥	🟥	🟥																									
Preliminary Research Work and Literature Review			🟥	🟥	🟥	🟥																						
Submission of Extended Proposal Defence						●																						
Preparation for Oral Proposal Defence							🟥	🟥																				
Oral Proposal Defence Presentation									●																			
Detailed Literature Review								🟥	🟥	🟥	🟥	🟥																
Catalysts Preparation										🟥	🟥	🟥			🟥	🟥	🟥											
Catalysts Characterization										🟥	🟥	🟥			🟥	🟥	🟥											
Preparation of Interim Report							🟥	🟥	🟥	🟥	🟥	🟥																
Submission of Interim Draft Report													●															
Submission of Interim Final Report														●														
Testing the Catalysts on Hydrocracker Rig															🟥	🟥	🟥	🟥	🟥	🟥								
Study Coke Formation on Spent Catalysts																	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥			
Analysis of Results																	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥			
Submission of Progress Report																					●							
Pre-SEDEX																								●				
Submission of Draft Report																									●			
Submission of Dissertation																										●		
Submission of Technical Paper																										●		
Oral Presentation																											●	
Submission of Project Dissertation (Hard Bound)																												●

● Key Milestone
🟥 Process

CHAPTER 4

RESULTS AND DISCUSSION

4. RESULTS AND DISCUSSION

4.1 Sizing

The prepared catalysts were sized using sieve shaker to obtain a standard range of size for the reaction. A standard range of catalysts size is very important as it will affect the production rate of the catalysts; therefore, to ensure a consistent production rate is obtained during the catalytic dehydration process, the catalysts need to be sized. After sizing the catalysts, the range is presented in *Table 5*.

Table 5: Range of catalysts' size

CAT 1 – 5	45µm - 125µm

4.2Characterization of Catalysts

4.2.1 Fourier Transform Infrared Spectroscopy (FTIR)

All the five catalysts have been sent for FTIR analysis to study the absorbance characteristic of the catalysts. Two different compositions for each alkaline earth oxide impregnated catalysts are compared with the basis catalyst to see the changes on the absorbance of the catalysts. The results are shown in *Figure 12* and *Figure 13*.

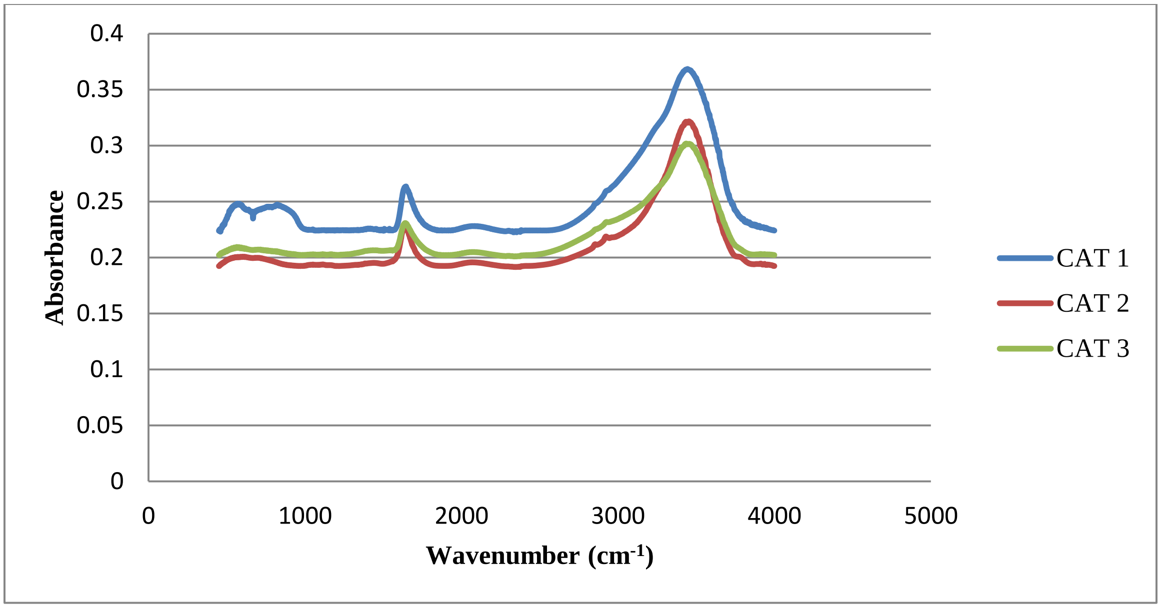


Figure 12: Comparison of absorbance of basis catalyst with Ni-MgO/Al_2O_3 with different composition of MgO.

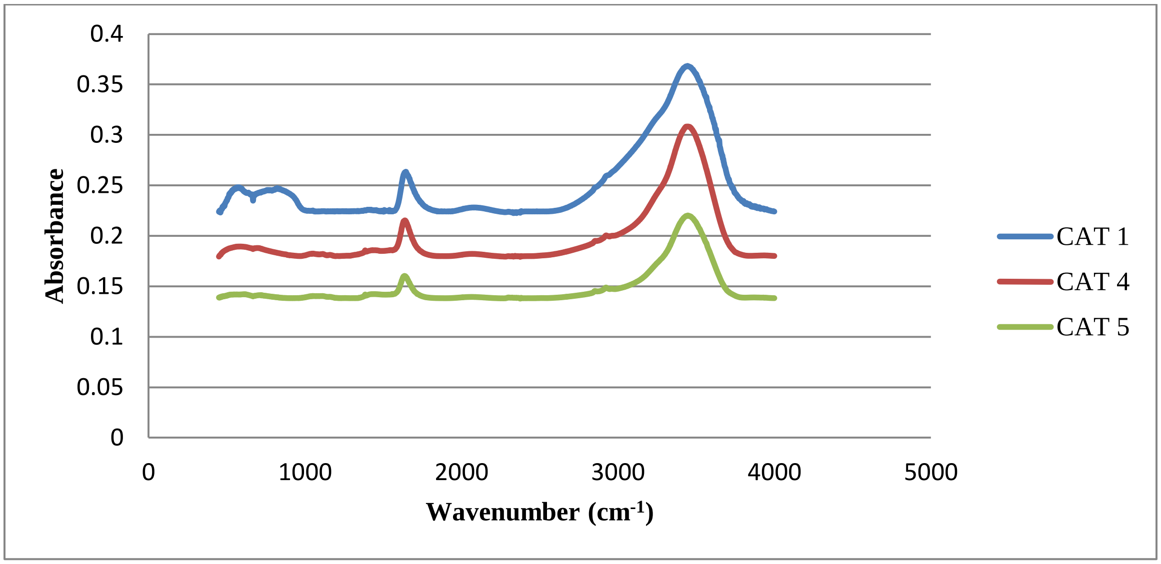


Figure 13: Comparison of absorbance of basis catalyst with Ni-CaO/Al_2O_3 with different composition of CaO.

From the results obtained, it is clear that the absorptivity of the catalysts is decreased with metals impregnated on it. The absorptivity is directly proportional to the absorbance.

$$A = abc \qquad (5)$$

Whereby, A = absorbance

a = absorptivity

b = pathlength

c = concentration

The decrease of absorbance is highly due to the blockage of the surface of catalyst by the presence of nickel, magnesium oxide and calcium oxide metals which directly reduced the absorptivity of the catalysts as well. From *Figure 12 and 13*, there are peaks appeared at wavenumber 3480cm^{-1} and 1680cm^{-1} which represent the stretching vibration of structural –OH and adsorbed water respectively (Rahemi, Haghighi, Babaluo, Jafari, & Estifaee, 2013). The increase of weight percent of metals impregnated on the alumina show the reduce of area of two peaks which mean the strength of stretching vibration of structural –OH and adsorbed water are reduced with metals impregnated on the catalyst. These characteristics of catalysts will help accelerating the carbon oxidation and reducing the coke deposition(Sánchez-Sánchez, Navarro, & Fierro, 2007).

4.2.2 Thermogravimetric Analysis (TGA)

One of the prepared catalysts is tested with thermogravimetric analysis to study the decomposition of catalyst with increasing temperature at three different heating rates. The selected catalyst is CAT2 and the results are presented in *Figure 14* and *Figure 15.*

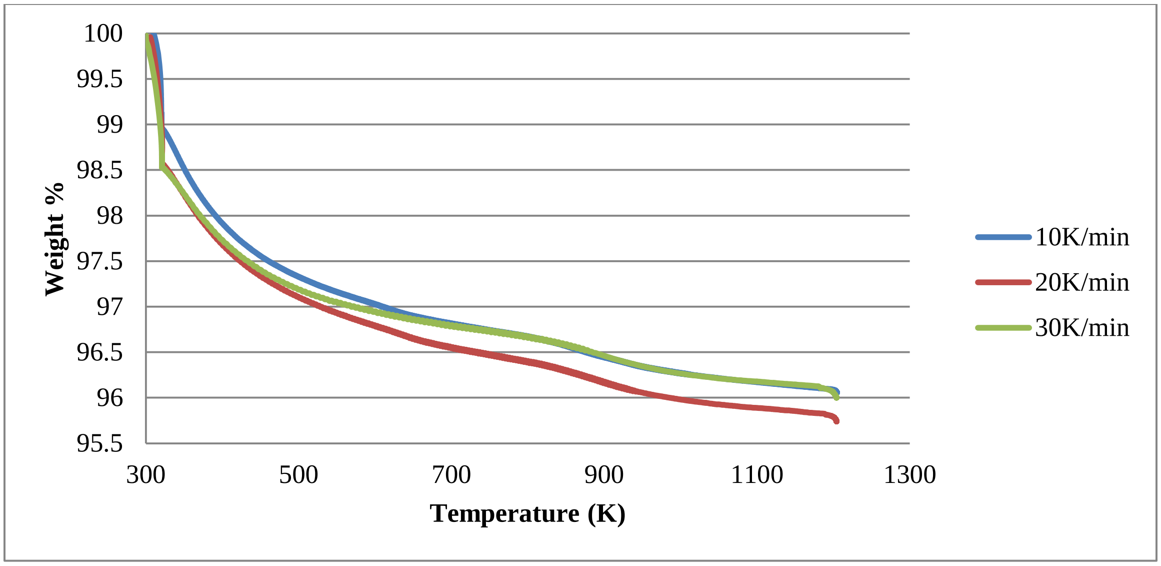


Figure 14: TGA results with weight% decomposed versus temperature for CAT 2 at three different heating rates.

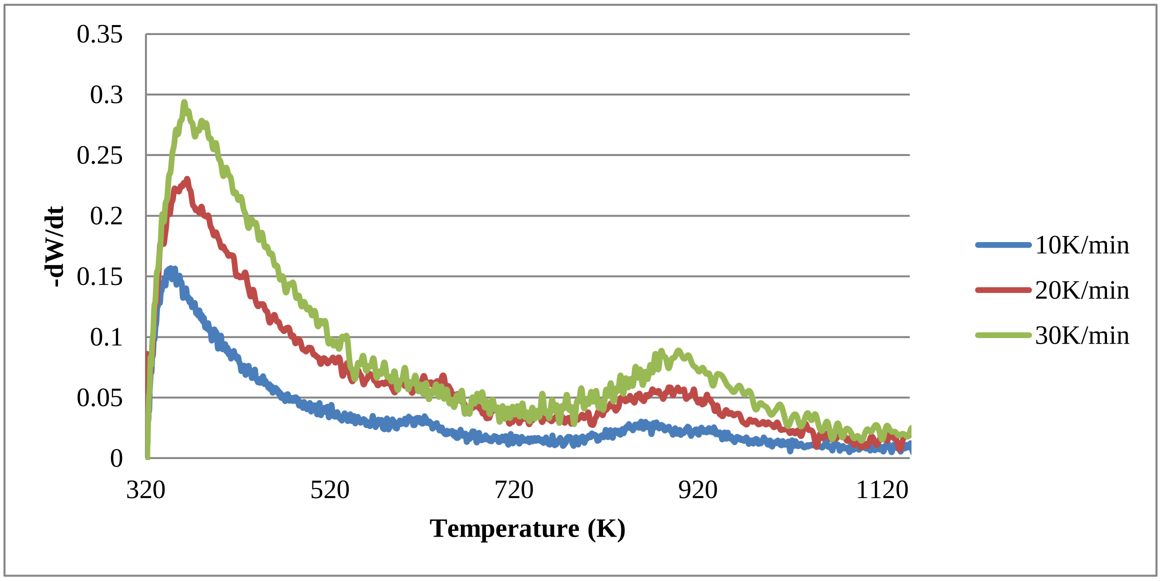


Figure 15 : TGA results with –dW/dt versus temperature for CAT 2 at three different heating rates.

From *Figure 14*, it can be seen that the catalyst is very stable as only about 5 wt% of catalyst been reduced even at the temperature of 1173K. By comparing the three heating rate, the catalyst under heating rate of 20K/min are able to decompose slightly more compared to the other two heating rates. Comparing the three different heating rate, it is found that the higher the heating rate, the higher the rate of decomposition of catalysts.

When the catalyst is compared with differential weight loss over time against temperature as shown in *Figure 15*, it is observed that the catalyst has a highest weight loss rate at around 363K and a moderate weight loss rate at around 895K which mean there are certain components in the catalyst have been decomposed greatly at that particular. As the TGA analysis was carried out with 100% flow of argon gas, there will only have decomposition occurred in the process, therefore there will be no weight loss due to oxidation and reduction. After further analysis, there is high possibility the decomposition of $Mg(NO_3)_2$ and $Ni(NO_3)_2$ occurred at the first and second peaks observed in *Figure 14* respectively. These can be represented by the equation below:

$$2Mg(NO_3)_2 \rightarrow 2MgO + 4NO_2 + O_2 \qquad (6)$$

$$2Ni(NO_3)_2 \rightarrow 2NiO + 4NO_2 + O_2 \qquad (7)$$

The decomposition of $Mg(NO_3)_2$ and $Ni(NO_3)_2$ forming MgO and NiO might be the reason causing the reduction of catalyst's weight. *Figure 16* shows the plot of temperature and weight over time which will give a clearer view of relation between temperature, weight and time for TGA analysis of catalyst. The dissection shows the two different stages of weight loss that occurred at two different times.

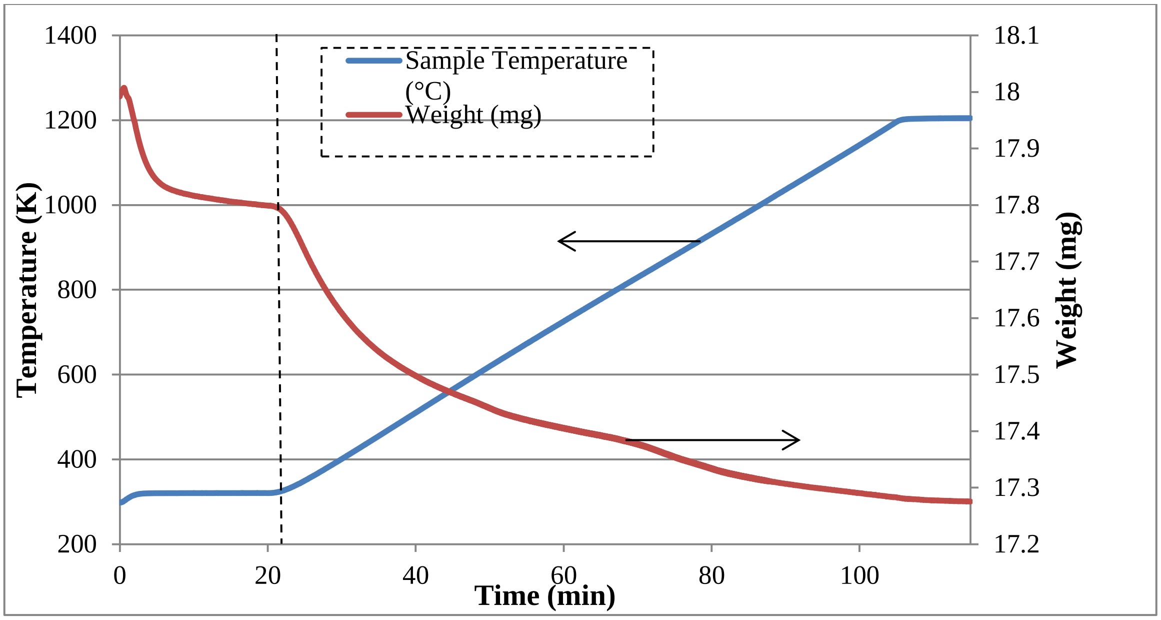


Figure 16: Graph of temperature and weight over time for CAT2 at 10K/min of heating rate

4.2.3 Field Emission Scanning Electron Microscopy (FESEM) Analysis

CAT2 was also been sent for FESEM analysis. A clear image of the surface of catalyst with impregnated metals on the surface was observed on FESEM micrographs as shown in *Figure 17* and *Figure 18.*

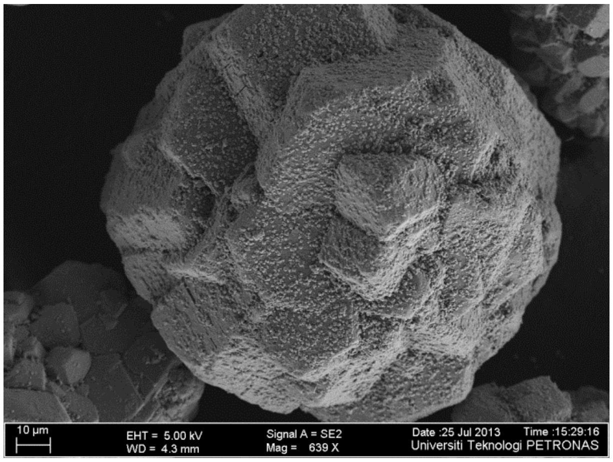


Figure 17: FESEM image (overview of catalysts)

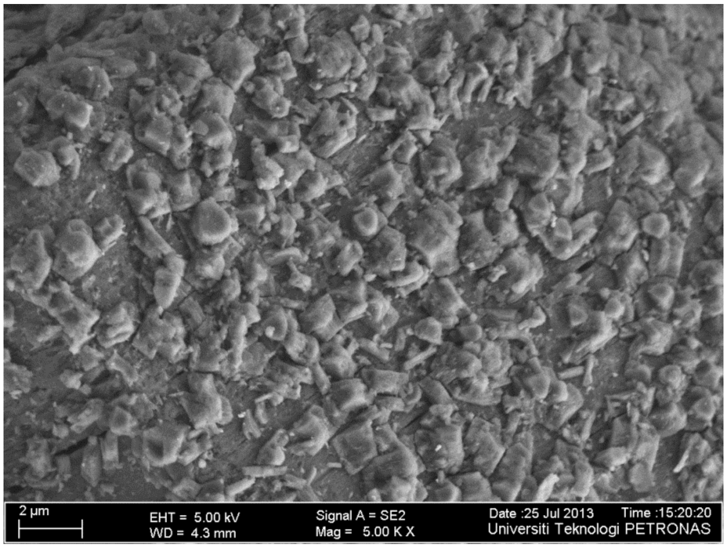


Figure 18: FESEM image (surface of catalyst)

4.2.4 Energy Dispersive X-ray (EDX) Analysis

The EDX dot-mapping of CAT2 is illustrated in *Figure 19*. All of the elements used in the synthetic procedure can be observed in the EDX spectrum. From this analysis, it shows that the Ni and Mg are uniformly dispersed in the form of small particles on the surface of alumina catalysts. *Table 6* shows the weight percentage of each element identified from the analysis and it is compared with the required amount calculated manually. From the table, it shows that the actual weight percentage of Ni and Mg impregnated on the catalyst is very close to the required value which proved that the catalyst is successfully synthesized.

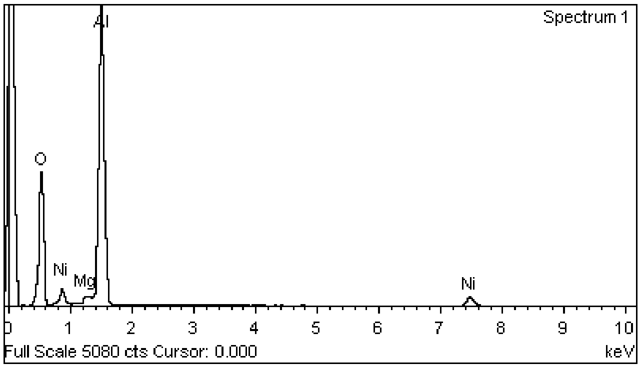


Figure 19: EDX dot mapping analysis of Ni-MgO/Al_2O_3 (CAT2)

Table 6: Composition analysis for each element in CAT2

Element	Weight%	Atomic%	Weight% w/o O	Required Weight%
O K	50.98	65.46	-	-
Mg K	0.86	0.73	1.75	2
Al K	41.24	31.40	84.13	88
Ni K	6.92	2.42	14.12	10
Totals	100.00		100	100

4.3 Study the effectiveness of catalysts on catalytic dehydration of ethanol

In this research, a commercial ethanol was used in replace to the bioethanol to carry out the experiment. Both liquid and gas sampling that taken out after the reaction were sent for GC-MS analysis to test the content of ethylene. Due to unavailability of standard ethylene, the actual concentration of ethylene in the samples weren't been able to identify. Therefore, the amount of ethylene content in the samples were estimated based on the area percentage under the peak of ethylene that been identified by GC-MS and the results are shown in *Table 7*.

Table 7: Content of ethylene in samples collected after reaction

Catalysts	Ethylene Production Area Percentage, %
CAT 1	42.90
CAT 2	42.89
CAT 3	49.77
CAT 4	69.12
CAT 5	65.36

There was no ethylene content detected in the liquid samples. This can be explained as ethylene is a very volatile substance which appears in gas form even at low temperature. So all the ethylene produced from catalytic dehydration was collected in gas form. From the table, it shows that catalysts impregnated with CaO have a higher overall production rate as compared to basis and catalysts impregnated with MgO. CAT 4 with

2wt% of CaO has the highest ethylene production with area percentage of 69.12%. While the basis alumina catalyst and catalyst with 2 wt% MgO has the lowest production rate.

4.4 Coke formation studies

4.4.1 Total carbon content by CHNS

The results obtained from total carbon content analysis via CHNS are presented in *Table 8*.

Table 8: Data collected from total carbon content analysis on spent catalysts

Catalysts	Carbon Content (wt%)			
	Before	After	Increment	Average
CAT 1	0.153	0.580	0.427	0.407
	0.158	0.544	0.386	
CAT 2	0.171	1.098	0.927	1.119
	0.149	1.459	1.310	
CAT 3	0.174	1.155	0.981	1.371
	0.174	1.935	1.761	
CAT 4	0.380	2.120	1.740	1.644
	0.429	1.977	1.548	
CAT 5	0.506	1.831	1.325	1.323
	0.521	1.901	1.380	

From the results, CAT 1 has the lowest carbon content this is because of the absence of Ni. Nickel is a metal that has high activity for hydrogenation(Elias et al., 2013) which helps in the combination of hydrogen atoms adsorbed on the catalyst surface and contributed to the reaction process but it also favors coke deposition(Vizcaíno et al., 2008). With the absence of Ni in the basis catalyst, the coke formation will reduce but at the same time the ethylene production rate will reduce as well. Comparing two alkaline earth oxide catalysts, catalysts impregnated with MgO(CAT 2 & 3) seem to have lower total carbon content as compared to CAT 4 and 5 that impregnated with CaO. This is due to the low production rate of ethylene for CAT 2 and 3, with a lower ethylene content of ethylene, it lowered the decomposition rate of ethylene forming coke. Further study need to be done to identify the reason behind the low production rate of ethylene for catalysts impregnated with MgO. From the results, CAT 4 and 5 that impregnated with CaO have average higher ethylene production rate and CAT 4 that contained 2 wt% of CaO achieved the higher ethylene content comparing to CAT 5 that has higher content of CaO (4wt%). This is because the CaO has basic property that will reduce the active site of catalysts, higher the content of CaO lower the total active site presence on the catalysts that allow the dehydration process to occur.

4.4.2 FESEM Analysis

The spent catalyst that chosen to send for FESEM analysis was CAT 2 which is same sample as the catalyst before the reaction to ease the process of making comparison on catalyst before and after the reaction. *Figure 20* shows the FESEM images taken before and after reaction for CAT 2.

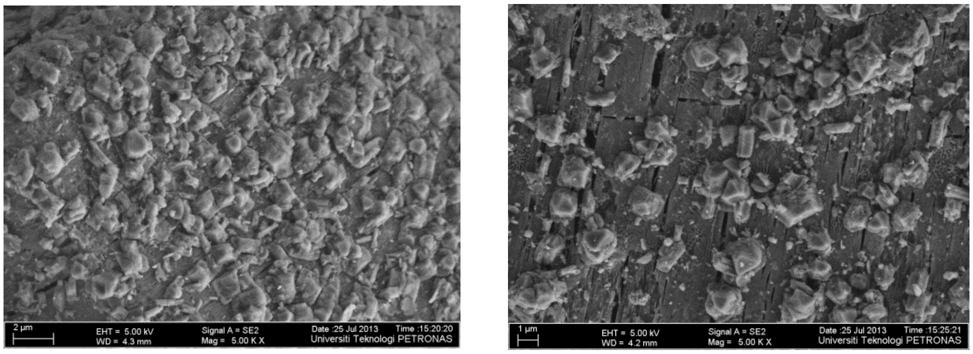


Figure 20: FESEM image for CAT 2 (left: before reaction; right: after reaction)

From the figure above, the surface of CAT 2 after the reaction seem to have fewer metals attached on it compared to the catalyst before reaction. This shows that there is some loss of metals in the reaction which might be one of the reasons causing the yield of ethylene for CAT 2 to be low.

4.4.3 EDX Analysis

The EDX analysis was applied on the same catalyst as FESEM which is CAT 2 to ease the comparison process. *Figure 21* shows the results obtained for the catalyst before and after the reaction.

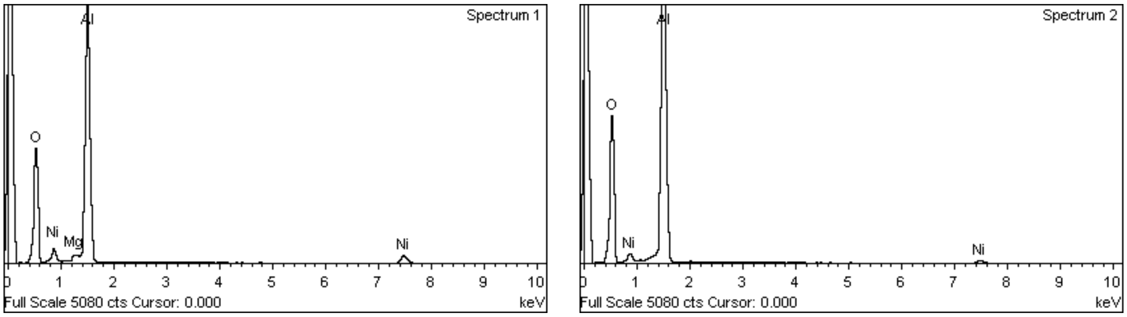


Figure 21: EDX analysis results for CAT 2 (left: before reaction; right: after reaction)

From the analysis, it can be seen that the alkaline earth oxide metal is loss after the reaction and less amount of nickel detected by EDX on the catalyst surface after the reaction. This result can be supported by FESEM analysis as less metals attached on the surface of alumina after the reaction. The loss of Ni and MgO might affect the yield of ethylene and coke deposition on the catalyst. This explained the decrease of ethylene yield and increase of carbon content for CAT 2.

Based on all the results obtained, it can be presumed that CAT 5 is the optimum catalyst for catalytic dehydration process whereby it is able to achieve an average of high ethylene production and low total carbon content after the reaction. However, detail studies need to be carried out to confirm the accuracy of the results obtained.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In a nutshell, the research is served to enhance the catalyst used in bioethanol dehydration to produce ethylene by increasing its resistance toward coke formation in the reaction which can strengthen the life span of catalyst, reduce the frequency of changing or regenerating the catalyst as well as reduce the overall operating cost of ethylene production using bioethanol dehydration process. The success of this research might lead to the replace of steam-cracking method in producing ethylene from natural resources by bioethanol dehydration whereby the bioethanol is produced from renewable resources. Eventually it helps to preserve and conserve the natural resources and prevent them from depletion.

In this research, alkaline earth oxide metals which contain basic property that can help prevent carbon deposition are impregnated on catalyst forming the bimetallic catalysts. There are two types of alkaline earth oxide used in this research which are Magnesium Oxide and Calcium Oxide. Different composition of these alkaline earth oxides were impregnated with nickel and alumina. The prepared catalysts were characterized by Sieve Shaker, FTIR, TGA, FESEM and EDX. The catalysts were tested on the catalytic dehydration process to produce ethylene from ethanol and the yield is obtained by sending the product to test on GC-MS. The spent catalyst is collected and studied for its total carbon content using CHNS to identify the amount of carbon deposited on the catalysts after the reaction. The yield of ethylene and amount of coke formation on catalysts after the reaction for each of the catalysts is compared and the catalyst with higher yield of ethylene and less amount of coke is selected to be the optimum catalyst. For this case, Ni-CaO/Al_2O_3 with 4 wt% of CaO (CAT 5) is chosen to be the optimum catalyst.

5.2 Recommendations

Due to the short time frame given for this research, a detail study on the research could not be carried out. There are spaces of improvements for this research in the future. In the future, there are some recommendations that are suggested and advices that student should follow if taking this research either for the next final year project's student or master student. This will ensure smooth research in the future with the fundamental knowledge obtained from this research studies.

For the characterization part, there are some characterization couldn't be able to carried out due to unavailability of the equipment that provided in the university. Therefore, in future student can try to characterize the sample using facilities from other research center or university if the facilities provided by own university is not sufficient. There are few characterization that student should be carry out in future that will help in this research such as BET analysis, XPS and H_2 chemisorption. Besides, student should try analyze the FESEM and EDX for all the other samples that been produced to have a clearer vision on the results obtained and make more reasonable justification provided there is no limitation on the usage of equipment.

In synthesizing catalysts using impregnation method, there is one suggestion from this research for research in future. In this research, both metals (Ni and alkaline earth metal oxides) were added to alumina one followed by the other and then only sent for drying and calcination. From the results obtained, this impregnation method seems to be unable to sustain the metals on the surface of alumina permanently. In future, student should try impregnate, drying and calcining of one metal first and repeat the same steps for the other metal on the same catalyst. It is believed that using this method could make the catalysts more stable. Furthermore, for further improvement student can try synthesizing the other alkaline earth metal oxides such as barium and strontium using the same method to study the difference of the results obtained from using other alkaline earth metals.

Last but not least, for the catalytic dehydration of ethanol to ethylene, in this research the product will have to collect separately and send it for GC-MS analysis which will take a lot of time and the samples will only be sent for analysis after all the experiments been carried out as the GC-MS analysis require booking. Thus, this caused immediate action cannot be taken if there is problem with the product obtained and once there is problem occur, all the experiment will have to repeat again which consumed a lot of times. Therefore, to ease the process, there are one recommendation can be done which is to install an online GC that attached with the hydrocracker rig. This will ensure the product produced from the process is immediately been identified by the online GC and immediate action can be taken if there is problem on the product produced. This will shorten a lot of times for the student to run the experiment and obtain more accurate results.

REFERENCES

Bi, J.; Guo, X.; Liu, M.; Wang, X. High effective dehydration of bio-ethanol into ethylene over nanoscale HZSM-5 zeolite catalysts. Catal. Today ***2010****, 149, 143–147.*

Chen, G.W., et al., Catalytic dehydration of bioethanol to ethylene over TiO2/γ-Al2O3 catalysts in microchannel reactors. Catal. Today, 2007. ***125****(1-2): p. 111-119.*

D. Fan, D. J. Dai, H. S. Wu, Ethylene formation by catalytic dehydration of ethanol with industrial considerations. Mat.(2013), 6, 101-115

Elias, Kariny F. M., Lucrédio, Alessandra F., & Assaf, Elisabete M. (2013). Effect of CaO addition on acid properties of Ni–Ca/Al2O3 catalysts applied to ethanol steam reforming. International Journal of Hydrogen Energy, 38(11), 4407-4417. doi: http://dx.doi.org/10.1016/j.ijhydene.2013.01.162

F.B. Noronha, M. Schmal, C. Nicot, B. Moraweck, R. Frety, J. Catal. 1997, 168, 42.

F. Epron, F. Gauthard, J. Catal. 198 (2001) 309–318.

Gurgul, J.; Zimowska, M.; Mucha, D.; Socha, R.P.; Matachowski, L. The influence of surface composition of Ag3PW12O40 and Ag3PMo12O40 salts on their catalytic activity in dehydration of ethanol. J. Mol. Catal. A ***2011****, 351, 1–10.*

H.B. Calvin, Mechanisms of catalyst deactivation, Appl. Catal. A: General 212 (2001), 17-60.

H. Idriss, C. Diagne, J. P. Hindermann, A. Kinnemann, M. A. Barteau in Proceedings, 10th International Congrass on Catalysis, Budapest, 1992, Vol. Part C (Eds.: L. Guczi, F. Solymosi, P. Tetenyi), Elsevier, Budapest, 1992, p.2119.

K. Y. Koo, H. S. Roh, Y. T. Seo, D. J. Seo, W. L. Yoon, S. B. Park, Coke study on MgO-promoted Ni/Al_2O_3 *catalyst in combined* H_2O *and* CO_2 *reforming of methane for gas to liquid (GTL) process., Elsevier, Appl. Catal A: General 340 (2008), 183-190.*

Rahemi, Nader, Haghighi, Mohammad, Babaluo, AliAkbar, Jafari, MahdiFallah, & Estifaee, Pooya. (2013). Plasma Assisted Synthesis and Physicochemical Characterizations of Ni–Co/Al2O3 Nanocatalyst Used in Dry Reforming of Methane. Plasma Chemistry and Plasma Processing, 1-18. doi: 10.1007/s11090-013-9460-x

R. Melendrez, G. Del Angel, V. Bertin, M.A. Valenzuela, J. Barbier, J. Mol. Catal. A 157 (2000) 143–149.

Sánchez-Sánchez, M. C., Navarro, R. M., & Fierro, J. L. G. (2007). Ethanol steam reforming over – (, La, Zr and Mg) catalysts: Influence of support on the hydrogen production. International Journal of Hydrogen Energy, 32(10–11), 1462-1471. doi: http://dx.doi.org/10.1016/j.ijhydene.2006.10.025

True, W.R. Global ethylene capacity continues to advance in 2011. Available online: http://www.ogj.com/articles/print/vol-110/issue-07/special-report-ethylene-report/global-ethylene-capacity.html (retrieved on 23 February 2013).

Vizcaíno, A. J., Arena, P., Baronetti, G., Carrero, A., Calles, J. A., Laborde, M. A., & Amadeo, N. (2008). Ethanol steam reforming on Ni/Al2O3 catalysts: Effect of Mg addition. International Journal of Hydrogen Energy, 33(13), 3489-3492. doi: http://dx.doi.org/10.1016/j.ijhydene.2007.12.012

V.R. Choudhary, B.S. Uphade, A.S. Mamman, Catal. Lett. 32 (1995) 387-390.

Warren R. True, Oil and Gas Journal, 2012, vol 110, issue 7

W. L. Gao, R. C. Jin, J. X. Chen, X. X. Guan, H. S. Zeng, F. X. Zhang, N. J. Guan, Titania-supported bimetallic catalysts for photocatalytic reduction of nitrate, Elsevier, Catal. Today. 90 (2004) 331-336.

Zaki, T., Catalytic dehydration of ethanol using transition metal oxide catalysts. Journal of Colloid and Interface Science, 2005. ***284****(2): p. 606-613.*

Zhang, Xian, Wang, Rijie, Yang, Xiaoxia, & Zhang, Fengbao. (2008). Comparison of four catalysts in the catalytic dehydration of ethanol to ethylene. Microporous and Mesoporous Materials, 116(1–3), 210-215. doi: http://dx.doi.org/10.1016/j.micromeso.2008.04.004