Preparation and characterization of Fe/Al_2O_3 catalyst for steam reforming of ethanol

by

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Dissertation Submitted in Partial Fulfillment of
the Requirement for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

DECEMBER 2010

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
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in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

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Tronoh, perak
July 2010

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.

OLIVER M. GORRES

Acknowledgement

I would like to seize this opportunity to thank to all parties who has contributed along the process in finishing the project. Special acknowledgment to all people who help me a lot in completing and finishing this Final Year Project, specifically:

1. Dr. Suriati binti Sufian– *Author's Supervisor*
2. Dr. Khalik Mohamad Sabil – *FYP Coordinator*
3. Dr. Anita Ramli– *Author's* Co-*Supervisor*

Besides that, I would like to thank Universiti Teknologi PETRONAS (UTP) and my lecturer, Dr. Suriati Sufian who have gave a lot advices and useful information as a guide for me in completing this project.

Apart from that, I would to express my gratitude to all the UTP lecturers who has been really helpful and understanding. Lastly, thank you to everyone who has contributed directly or indirectly in completing my Final Year Project.

Abstract

This project is mainly about the preparation of the alumina supported catalyst for the steam reforming of ethanol. The catalyst which needs to be prepared is Fe/Al_2O_3. Mostly in industry steam reforming is mainly used for methanol and ethanol which source from the natural gas. This process widely used to obtain hydrogen gases which are one of the alternative sources of energy for fuel oil. The main problem in this project is how to prepare the Fe/Al_2O_3 catalyst in a lab scale and to do the characterization of the catalyst itself. To obtain a well structured catalyst, a thorough research on the method of preparation is made which the scope covers mostly about precipitation and impregnation method. Both precipitation and impregnation methods have different steps in preparation which leads to the same output product which is the catalyst. Impregnation method will have the prepared solution having the metal precursor to fill in the pore structure of the support bodies while precipitation process consist of preparation of the support itself from the molecular level then follows the same steps in impregnation method. From the findings throughout certain researches in the industrial production, impregnation method implies better result in a lab scale production. Thus, further studies in impregnation method are required for the preparation of catalyst through experiment. Once the procedure and operating parameters are identified, then the experiments for the catalyst preparation will be conducted.

TABLE OF CONTENT

Contents **Page no.**

Chapter 1 : Introduction

Chapter 2 : Literature review

Chapter 3 : Methodology

Chapter 4 : Result and Discussion

Chapter 5 : Conclusion

LIST OF FIGURES

LIST OF TABLE

CHAPTER 1

INTRODUCTION

1.1 Introduction

In this modern day, the advancement of technology and infrastructure has created an environment which simplifies our daily activities and even in our social lifestyle. Although there are improvements but still our energy sources is depleting as years passed by [20]. Fuel as in gas fuel or liquid fuel is still our main sources of energy that has been decreasing throughout the years and now facing the problem of finding alternative to be replaced. One of the potential energy that has been going through research is the hydrogen energy fuel which is in the form of fuel cells [19]. It is mentioned that the fuel cells can provide a clean energy source for automotive applications as the alternative for gasoline and diesel engines. Based on agriculture, raw materials such as cassava, molasses and corn are available for fermentation to produce dilute ethanol solution which is called bio-ethanol. Bio-ethanol contains 12 wt% of ethanol which is variedly used as an alternative fuel or feedstock for producing chemicals such as ethylene, acetaldehyde and acetone [21].

1.2 Problem statement

Throughout the current steam reforming process which industrially practiced nowadays, there are many catalyst used for the process. The catalysts help to enhance the reaction on the process during the water gas shift phase. In this project, an alumina supported catalyst will be synthesized and will be undergo several characterization techniques. The only matter is how to determine the best method of preparation for the catalyst and how to obtain the characteristic of the catalyst.

1.3 Background

In recent years, research has been made to develop the processes of obtaining rich-hydrogen gases through ethanol steam reforming. Ethanol also known as ethyl alcohol is a volatile, flammable and colourless liquid [4]. It is a type of alcohol found in the alcoholic beverages and in modern thermometers. Ethanol molecular formula is C_2H_6O and is often abbreviated as EtOH, using the common organic chemistry notation of representing the ethyl group (C_2H_5) with Et. During these days, ethanol which is widely used for industrial purposes is also produced as by-products of petroleum refining [16]. On the other hand, steam reforming refers to a process which major importance for hydrogen production and synthesis gas for several decades. Classically, steam reforming process involves converting of methanol and other hydrocarbons in natural gas to hydrogen and carbon monoxide by reaction of steam with nickel catalyst on a ceramic support [9]. The production of hydrogen from methanol is always referred to Steam Methanol Reforming (SMR) and it requires natural gas as feedstock. However, as SMR process is widely applied in the industry, the demand of the natural gases in other market sectors also tend to increase. This will result in decreasing of the reserve natural gases and the supply will be put under greater pressure [12]. Apparently, the natural gas prices will also increase. The drawback of the steam methanol reforming process is the production on carbon dioxide (CO_2) which emitted twice than the hydrogen produced. Considering the effect of SMR process to the economy and environment itself, thus, ethanol came as an alternative to methanol and the feedstock can be obtain not from the natural gas alone [17].

Steam reforming of ethanol process serves the same purpose as Steam Methanol Reforming which is producing hydrogen as a fuel cell. In steam reforming of ethanol, the process itself is quite similar with SMR process. Ethanol as the feedstock will mix with the steam in a considerable ratio of ethanol to steam. The possible reaction would be [13]:

$$C_2H_5OH + H_2O = CH_4 + CO_2 + 2\ H_2$$

$$CH_4 + H_2O = CO + 3\ H_2$$

$$CO + H_2O = CO_2 + H_2$$

The mixture of ethanol and steam will produce methane, carbon dioxide and hydrogen gas. Methane which was produced in the first reaction will then further the reaction to produce carbon monoxide and hydrogen gas. Carbon monoxide that been produce from the second reaction will reacted with steam over a catalyst to produce hydrogen and carbon dioxide. The catalyst that had been widely used is such as Rh/Al_2O_3 , Ni/La_2O_3 , ZnO , Co/Al_2O_3, Cu/SiO_2 combined with Ni/MgO , Cu, Ni, Pt,or Rh on various supports , potassium promoted Ni/Cu , and dual bed Pd/C Ni/alumina systems [10]. These catalyst have been going through experiments and research in order to obtain the active catalyst for water gas shift phase during the process. Each catalyst has their own chemical and physical properties which react upon few factors that involve. Thus, further research is needed to identify the most active catalyst which can contribute in achieving higher purity of hydrogen through the steam reforming of ethanol process [11].

1.4 Objective

The main objective of this project is to prepare an alumina support catalyst which is Fe/Al_2O_3 and to study the characterization of the catalyst. This catalyst purposed to be used in the steam reforming of ethanol which will enhance the reaction that take place in the process to produce higher purity of hydrogen.

The project objectives include:

1. To determine the best method that will be used for the catalyst preparation. There are many methods that had been applied to prepare a catalyst throughout the industry.

2. To synthesize Fe/Al_2O_3 catalyst. The production of Fe/Al_2O_3 catalyst will be conducted after the best method has been determined.

3. To do a characterization on the catalyst. The catalyst will be prepared using the most preferred method.

4. To apply the catalyst in the steam reforming of ethanol. In this project, the prepared catalyst (Fe/Al_2O_3) will be determine whether the catalyst is potentially to be used in the ethanol steam reforming process to produce higher purity of hydrogen. Thus the catalyst must be high activity, selectivity and stability.

In conclusion, this project focus more on the preparation of the catalyst and the compatibility in its characteristic which will be use in ethanol steam reforming for hydrogen production.

CHAPTER 2

LITERATURE REVIEW

2.1 Methods of catalyst preparation

The aim of this catalyst preparation is to obtain a catalyst which can be employed in the ethanol steam reforming for hydrogen production purpose. The catalyst preferred to be high activity, selectivity and stability [3]. In this case, the iron (Fe) must be sufficient enough to be highly dispersed on the support (Al_2O_3) which results in large contact area during the reaction. In order to achieve this result, the active metal are usually deposited on the surface of the support which has high porosity and be able to increase the stability of the catalyst and hence the catalyst life [4]. Below is the common preparation method that has been applied in the industry.

2.1.1 Impregnation method

This procedure requires the support to get contact with an amount of solution that contains the metal precursor then it is dried and going through calcinations. There are two types of impregnation which can be referred. The first one is called "incipient wetness" or "dry impregnation" [14]. This type of impregnation required a volume of solution containing the metal precursor same with the pore volume of the support. The impregnation can be performed rapidly since the uptake of the liquid to the support body proceeds fast [12]. The concentration gradient between the support and the solution allows the liquid to be absorbed faster into the support bodies. It is mentioned that this method is widely used in the industry as it is simple and economical especially when it requires costly active components. Dry impregnation method requires a thorough calculation of the pore volume of the support and the solution. It is also important to have a high concentration of metal precursor in the solution to achieve highly active catalyst. Errors in determining the suppose concentration of the solution and the volumes lead to an unfavourable distribution of the active metal on the support bodies. The second type of impregnation method is called "wet" or "soaking" impregnation [13]. This type of impregnation involves the use of an excess solution containing the metal precursor on the support. The support is then left for a long period of time under stirring and then later will be dried and calcinated. When a solution of larger volume than the pore volume of the support bodies contacts, the metal precursor present in the liquid phase out of the support bodies must diffuse into the pores of the support because the flow does not proceed [14]. But the liquid diffusion is slow and will take hours to obtain same concentration between the support and the solution.

2.1.2 Precipitation method

*Precipitation method consist of 2 steps of preparation which is co-*precipitation and deposited precipitation. Co-precipitation is commonly used to produce support of the catalyst that will be used in deposited precipitation but still the component of the support will also have the active metal of the catalyst [6]. This method that requires a preparation of solutions containing metal salt and a salt compound that will be mixed under stirring to be converted into support. Stirring will be performed under base in order to precipitate as hydroxides and/or carbonate. The mixed solution will be gone through ageing under certain temperature while stirring. After a period of time, the precipitate will then be washed with deionised water to remove the salt compound. Then the precipitate can be transformed into oxides by heating through preferred operating parameters [12]. In industry the choice of salt and alkali will most likely depends on the moderate cost, the solubility of the solvent (water), and most important, avoiding the introduction of compounds that can cause negative effect on the final catalyst such as chlorine ions which is well known as common poisons and their present must be avoided [13]. Through co-precipitation, a uniform distribution on a molecular scale of different active species in the final catalyst could be obtained. Unlike impregnation, co-precipitation tends to produce catalyst with its active metal and support formed on a molecular scale. Thus there are many variables that need to be considered such as the order of addition of the different solutions, the temperature, ageing time of the precipitate, the filtering and the washing procedure [15]. To gain higher concentration of the active metal in the support, we could proceed to the second step which is the precipitation deposition method. The support produced in the co-precipitation process will be then be crushed into fine particles and suspended in the de-ionized water. After that it will be mixed with the solution containing the active metal precursor in a desired amount. Generally, the principle is similar with the co-precipitation method, except this method involves liquid diffusion into the pore of the support [14]. The drawback of this method is that the precipitation on the metal hydroxides particles inside the pores of the supports is difficult thus the nucleation and growth on the support will not have a uniform distribution. Thus rapid growth in the solution bulk will result in a formation of large crystallites at the surface of the support. Since the large particle cannot enter the pores, it will be deposited at the external surface of the support [16]. In order to prevent this problem, slow addition of the alkali solution is needed to control the nucleation growth and also to maintain the ph level in the solution. Research has been made and it is identified that the best base to perform a uniform distribution of the active metal on the support is urea.

2.1.3 Drying

Drying which follows after impregnation and precipitation purpose to cause the evaporation of the liquid solvent. Catalyst usually will be dried at the temperatures between 80°C to 200°C [2]. As the catalyst undergoes drying process, it is stated that the liquid solution inside the pore structure of the catalyst is transported by the capillary flow. This phenomenon will actually redistribute the precursor by adsorption/absorption process. There are total 3 stages of drying which consist of preheating period, constant-rate period and falling-rate period. Preheating period tends to heated up the support by the drying medium [12]. The rate of drying increases as the temperature increases. After that, constant-rate period follows with higher temperature. It purposed to remove the vapour from the supports saturated surface. During this time, the capillary flow of the moisture inside the support is still sufficient to keep the surface saturated, which helps to distribute the metal precursor. At this rate, the rate of drying is depending on the rate of heat transfer to the evaporating surface and the temperature of the saturated surface is constant which is also called as wet-bulb temperature [18]. Wet-bulb temperature can be defined as the lowest temperature that can be reached by the evaporation of water only. This stage also helps to transport the liquid to the external surface of the support through capillary flow inside the support. For the final stage, the falling-rate period occurs when the moisture in the pores of the support is no longer be able to keep the surface saturated and the drying rate decreases [2]. Dry patches begin to appear near the surface and the temperature begins to rise. At this stage vaporization takes place inside the solid. At the same time, vapour convection flows begin to dominate the liquid transport inside the support and the dispersion of the precursor is negligible [12]. Thus, from the 3 stages of drying, it is shown that in order to eliminate the solvent leaving the precursor in the support, different variables need to be focused such as the rate of heating, final temperature , type of atmosphere and the time treatment can contribute to varies in catalyst quality in terms of active metal distribution.

2.1.4 Calcination

In the catalyst preparation, calcinations follow after drying process. Calcination is a thermal treatment process applied to ores and other solid materials in order to bring about a thermal decomposition, phase transition, or removal of a volatile fraction. The calcination process normally takes place at temperatures below the melting point of the product materials [1]. This treatment requires heating of the catalyst in an oxidizing atmosphere at a high temperature that can reach until 450°C. The purpose of calcinations is to decompose the metal precursor with formation of an oxide and also removal of the gaseous product [4]. Calcination also tends to decompose the cations and anions which previously introduced during the early stage. Thus, reduce the weight of the metal supported catalyst. In industrial production, calcinations is useful for the removal of the extraneous material, like binder or lubricants which have been used during previous forming operations. In the case of alumina support catalyst, calcinations performed at the temperature around 500°C to 600°C [1]. The high temperature can give rise to the reaction with divalent metal oxides such as Ni, Co and Cu with consequent formation on the surface metal. Thus, higher temperature needed for reduction than that needed for the oxides. When dealing with the bimetallic catalyst, the calcinations temperature should be control in order to avoid formation of two separates oxide and the segregation on one of the component [8].

2.1.5 Effect of Drying

Supported catalysts are used for a wide variety of reactions, and are the most frequently used types of catalysts. The porous support, typically alumina support, which is designed to disperse the active component such as Iron (Fe) also provides thermal and mechanical stability, and reduces the amount of the active component [4]. The preparation of supported catalysts generally involves three steps: impregnation (wet incipient impregnation) of precursor to the support body, (2) removal of the liquid solvent such as drying, and (3) transformation of the precursor into its desired form by calcination. Frequently, pre-treatment in the reactor is required to obtain the active form of the catalyst such as reduction by H2 or CO [12]. Deposition of the active component (metal) is typically done by impregnation, often involving aqueous solutions. If the support surface is hydrophobic or if hydrolysis of the support must be avoided, a non-aqueous solution is used. During the impregnation step, the support is immersed in a solution of the inert precursor. In the case of capillary impregnation, the support is initially dry, while during impregnation [13], the support is initially filled with the liquid solvent. In both cases air can be trapped in the pore volume of the particle, which may hinder impregnation. As the liquid penetrates the support due to capillary pressure, the entrapped air is compressed. The liquid penetration ends when the capillary pressure is equal to the pressure of the entrapped gas .If the pore radius is very small, the capillary pressure is much larger than the pressure of the entrapped air and air removal will not lead to any appreciable differences in the results. At the end of the impregnation step the distribution of the precursor in the support is typically a function of the metal/surface interaction (adsorption), the pore structure, and the diffusivity of the dissolved precursor in the impregnating solution [16].

2.2. Analysis Techniques

Certain equipments will be used for the characterization analysis of the catalyst. The characterization will mostly consist of the physical and chemical properties of the catalyst. A series of test will be conducted on the catalyst through special equipments to obtain the data on the catalyst. Below is the possible technique for the characterization analysis.

2.2.1 X-ray Diffraction (XRD)

A Diffractometer is a measuring instrument for analyzing the structure of a material from the scattering pattern produced when a beam of radiation or particles (as X rays or neutrons) interacts with it. Because it is relatively easy to use electrons or neutrons having wavelengths smaller than a nanometre, electrons and neutrons may be used to study crystal structure in a manner very similar to X-ray diffraction[24]. Electrons do not penetrate as deeply into matter as X-rays, hence electron diffraction reveals structure near the surface; neutrons do penetrate easily and have an advantage that they possess an intrinsic magnetic moment that causes them to interact differently with atoms having different alignments of their magnetic moments. Powder defraction (XRD) is a technique used to characterise the crystallographic structure, crystallite size (grain size), and preferred orientation in polycrystalline or powdered solid samples[24]. Powder diffraction is commonly used to identify unknown substances, by comparing diffraction data against a database maintained by the International Centre for Diffraction Data. It may also be used to characterize heterogeneous solid mixtures to determine relative abundance of crystalline compounds and, when coupled with lattice refinement techniques, such as Rietveld refinement, can provide structural information on unknown materials[27]. Powder diffraction is also a common method for determining strains in crystalline materials. An effect of the finite crystallite sizes is seen as a broadening of the peaks in an X-ray diffraction as is explained by the Scherrer Equation.

2.2.2 Scanning Electron Microscope (SEM)

The **scanning electron microscope** (SEM) is a type of electron microscope that scans the samples with high energy beams and produce images of the sample surface structure in a pattern. The electrons that been shot to the samples will interact with the atoms and produce result such as structure and composition of the samples. In the most common or standard detection mode, secondary electron imaging or SEI, the SEM can produce very high-resolution images of a sample surface, revealing details about less than 1 to 5 nm in size[27]. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. A wide range of magnifications is possible, from about 10 times to more than 500,000 times, about 250 times the magnification limit of the best light microscopes[25]. Back-scattered electrons (BSE) are beam electrons that are reflected from the sample by elastic scattering. BSE are often used in analytical SEM along with the spectra made from the characteristic X-rays. Because the intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen, BSE images can provide information about the distribution of different elements in the sample. For the same reason, BSE imaging can image colloidal gold immuno-labels of 5 or 10 nm diameter which would otherwise be difficult or impossible to detect in secondary electron images in biological specimens. Characteristic X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher energy electron to fill the shell and release energy. These characteristic X-rays are used to identify the composition and measure the abundance of elements in the sample[27]. Below are the example of catalyst that had been analyst using SEM method[28].

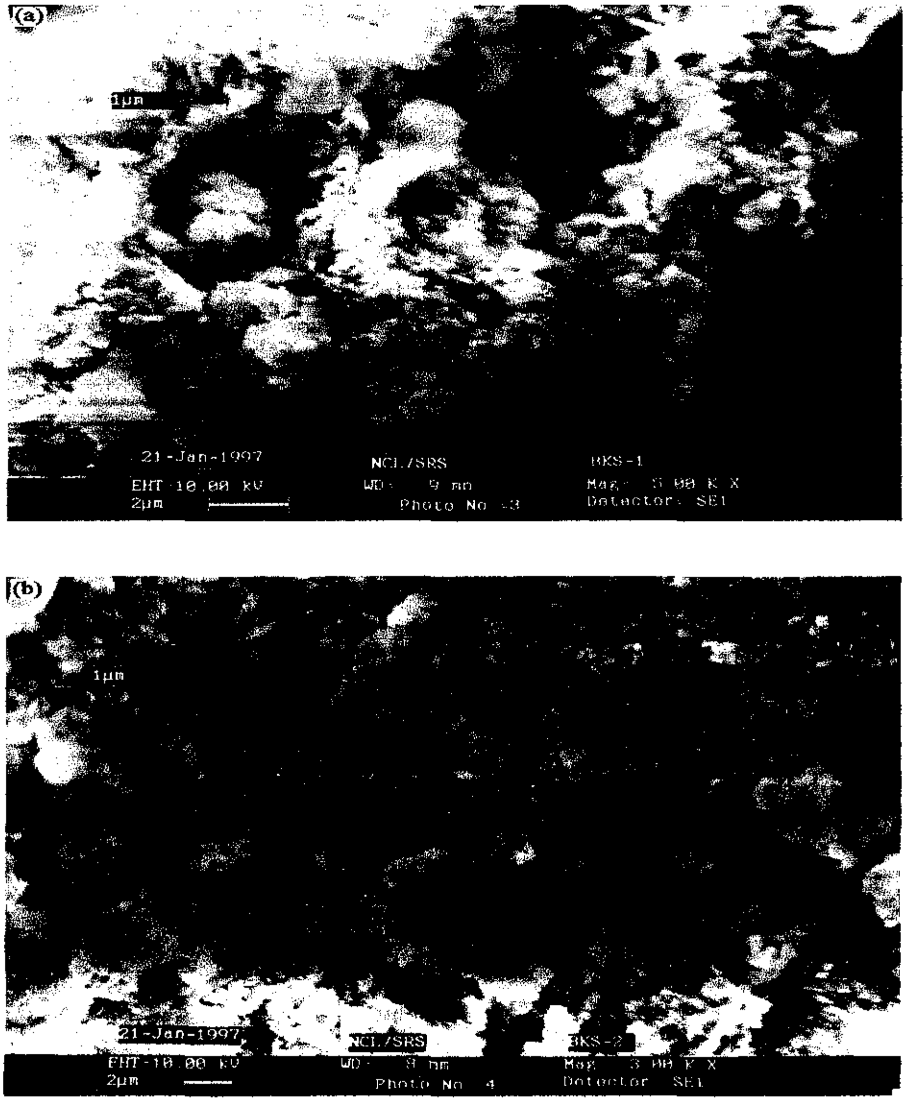


FIGURE 1: (a) SEM micrograph of unused Cat B. (b) SEM micrograph of used Cat B.

CHAPTER 3

METHODOLOGY

3. Methodology

In this project, it is determined that the best method to produce an alumina catalyst is by using wet impregnation method. Solution containing metal precursor (iron) will be prepared within a desired molarities. The support (alumina) will then be immersed in the solution for a period of time. When the support is being immersed, the solution will filled up the void (porous) inside the support and the surface of the support. After that, the support will be going through drying stage. In this case, the support will be heated up at a certain temperature. Then, the support will be calcinated under a high temperature to remove the remaining solvent inside and at the surface of the support. There are a few factors that can be manipulated during the experiment steps.

3.1 pH difference

Catalysts play a key role in industry which is why catalyst preparation plays an important role in catalysis research in the past years. The most preferred preparation method being impregnation, is focused on in the early steps of catalyst preparation. In this step a metal is contacted with an oxide with high surface area in hope to create small metal particles with large surface area. When choosing an oxide to contact with the metal, it must have a large surface area and be compatible with the corresponding metal. The first things that need to be determine is the point of zero charge (PZC) of the oxide. The PZC is a pH where the net surface charge of the oxide is zero. In solution, when the pH is greater than the PZC, the surface of the oxide is negatively charged and de-protonated. When the pH is less than the PZC, the surface of the oxide is positively charged and protonated. So oxides that are places in solutions with a pH greater than its PZC will absorb cations and oxides contacted with a solution with a pH less than its PZC will absorb anions. Thus, in this case, since the precursor is Iron (Fe^{3+}), so the solution made must be more than its PZC. This will allow the metal precursor to attach at the support body. The table below is the propose data that need to be taken during the experiment [5].

Table 1: Data used for PZC experiment

	Alumina
Surface area (m2/g)	0.8
Mass (g)	10

Sample	Acid/ Base added (ml)	Trial #	pH initial	pH final	Trial #	pH initial	pH final
1							
2							
3							
4							

3.2 Drying temperature

As *mentioned, drying purpose to increase the adsorption of the solution* containing the metal precursor into the support body and also to remove the solvent from the support. There are 3 stages that involve during the drying which is preheating period, constant-rate period and falling-rate period. The rate of drying is different for a given temperature and this will cause the difference in distribution of the metal precursor on the surface body. High temperature may lead to a faster drying rate but it also increase the chances cause less distributed of precursor on the support body. Besides, the support body itself may have spaces containing air, thus high temperature of a sudden will cause the formation of gases such as NH_2. On the other hand, low temperature may result slow drying rate and this might as well causing the metal precursor not well distributed. Thus, a proper temperature need to be determined in order to obtain well distributed catalyst.

Table 2: Data for alumina support drying rate

Sample	*Temperature (ml)*	*Trial #*	weight i (g)	weight f (g)
1				
2				
3				
4				

3.3 Calcination temperature

Calcination is a process purpose to remove the remaining solvent in the support. Usually calcinations will take place at a temperature as high as 350°C. This high temperature will ensure that the remaining component inside on the support will be completely removed. High temperature is needed because the component on the solvent might be difficult to determine. Unwanted component on the support body may result in less performance of the catalyst. In this experiment, the calcinations temperature will be varied from range 250°C to 350°C. The difference in calcinations temperature theoretically will affect the performance of the catalyst.

Table 3: Data for Alumina support calcination duration

Sample	Time (hour)	Trial #	weight i (g)	weight f (g)
1				
2				
3				
4				

3.4 Experiment

Equipments

1. 100mL beaker
2. Magnetic stirrer
3. Hot plate
4. Oven
5. Ceramic plate
6. Sample bottles

Chemicals

1. 10M Hydrochloric acid (HCl)
2. 0.1M Sodium hydroxide (NaOH)
3. Iron(III) nitrate, $Fe(NO_3)_3$
4. Alumina oxide, Al_2O_3

Experimental Procedure

A 5% Fe/ Al_2O_3 catalyst was prepared by impregnation (incipient wetness method) of Al_2O_3 (0.8 m^2/g) with a iron(III)nitrate solution with iron as precursor. There will be 9 samples prepared as shown in Table 4. All the samples were dried at 120°C and will be calcined at different temperature as shown in Table 5 for 24 hour. The pH value of each samples will be manipulated using 10M of HCl and 0.1M of NaOH. The samples will be left on a stirring condition before going through drying process.

The particle size distribution of iron on the alumina support will be obtained through the X-ray Diffraction(XRD) analysis and by Scanning Electron Microscope(SEM). XRD will be used to determine the characteristic of the catalyst such as the density as well as the particle distribution. Through the analysis, it will be possible to obtain the intensity of the catalyst itself through the analysis. On the other hand, SEM provide a high resolution on the catalyst in molecular level. This will help to give a better picture of the iron precursor distribution on the alumina support catalyst. SEM analysis will also give the percentage of metal surface area on the support.

Flow chart

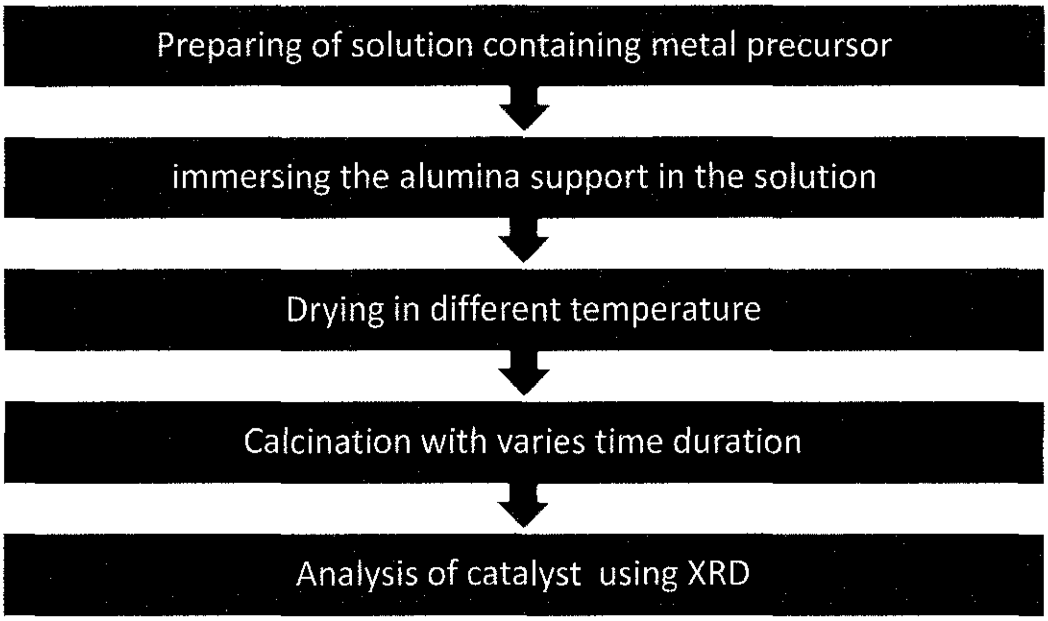


Figure 9: Methodology flow chart

CHAPTER 4

RESULT AND DISCUSSION

4.0 Experimental Result

	Alumina
Surface area (m2/g)	0.8
Mass (g)	10

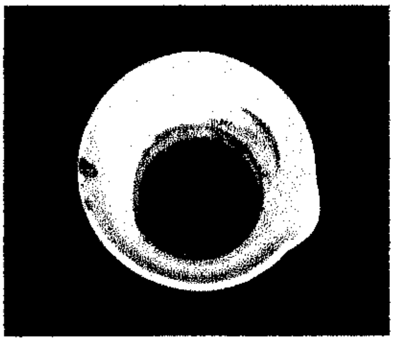
Table 4: loss of water after drying.

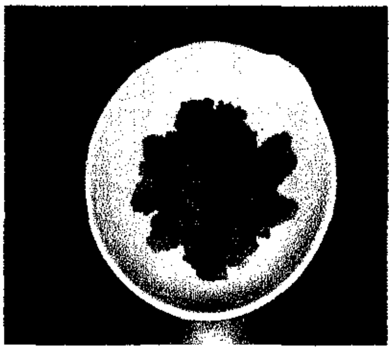
Sample	*pH target*	*pH initial*	*pH final*	Initial weight, w_i (g)	Final weight, w_f (g)	$w_i - w_f$ (g)
1	5	6.72	5.21	20.93	15.00	5.93
2	5	6.63	5.24	21.10	15.50	6.1
3	5	6.72	5.30	20.60	16.00	4.6
4	7	6.84	6.91	20.82	14.12	6.7
5	7	6.71	6.82	20.80	15.00	5.8
6	7	6.72	6.74	21.04	14.89	6.15
7	9	6.82	8.82	19.57	13.38	6.19
8	9	6.73	8.79	20.01	14.22	5.79
9	9	6.71	8.84	20.10	13.48	6.62

Table 5: loss of water after calcination.

Sample	Calcinations temperature (°C)	Initial weight, w_i (g)	Final weight, w_f (g)	$w_i - w_f$ (g)
1	350	49.50 -	48.67	0.83
2	400	50.20	49.10	1.1
3	350	50.81	49.03	1.78
4	400	51.09	49.26	1.83
5	350	47.35	46.49	0.86
6	400	47.80	46.88	0.92

Table 6: Sample observation after drying at 120°C

Samples	Observation
 $Fe(NO_3)_3 + Al_2O_3 + HCl$ pH 5.21	1. The sample are fragile white patches still can be seen. 2. Only the surface areas are hardened and have darker brownish colour than the bottom part.

 $Fe(NO_3)_3 + Al_2O_3$ pH 6.72	1. The sample are harder 2. The brownish colour tone is not equal. 3. The bottom parts of the sample are as hard as the surface.
 $Fe(NO_3)_3 + Al_2O_3 + NaOH$ pH 8.82	1. The sample are harder 2. The brownish colour tone is much more equal. 3. The hardness of the bottom part of the sample is the same as the top surface.

XRD result

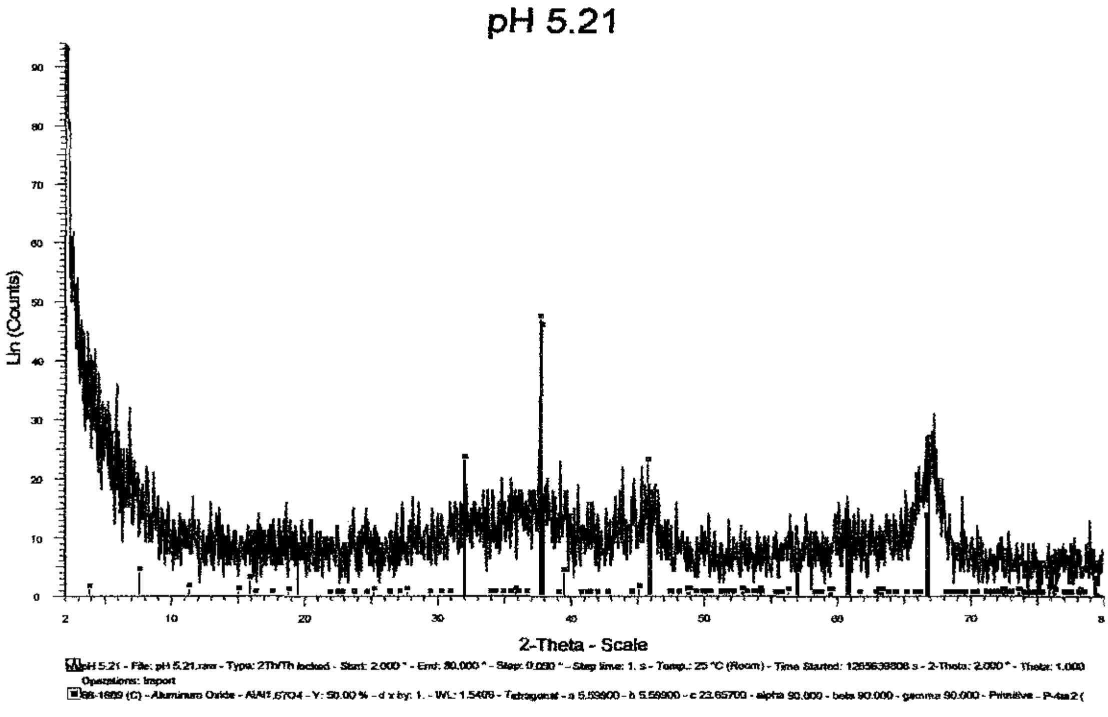

pH 5.21

FIGURE 2: X-ray Diffraction analysis for Fe/Al$_2$O$_3$ At pH 5.21.

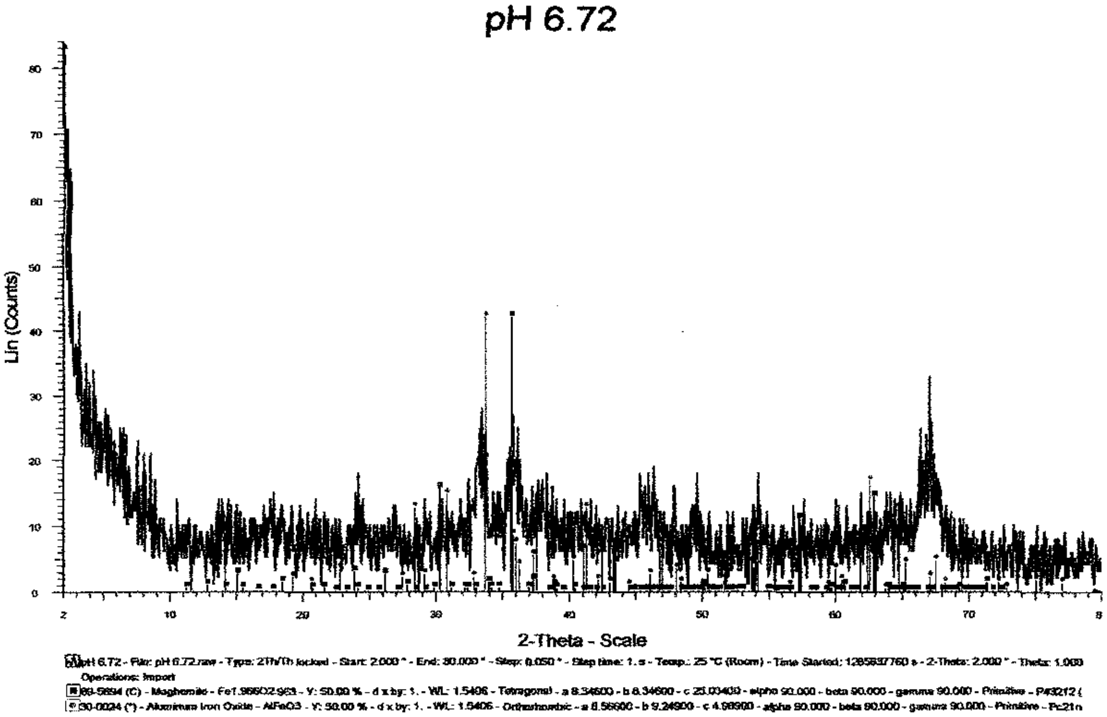

pH 6.72

FIGURE 3: X-ray Diffraction analysis for Fe/Al_2O_3 At pH 6.72

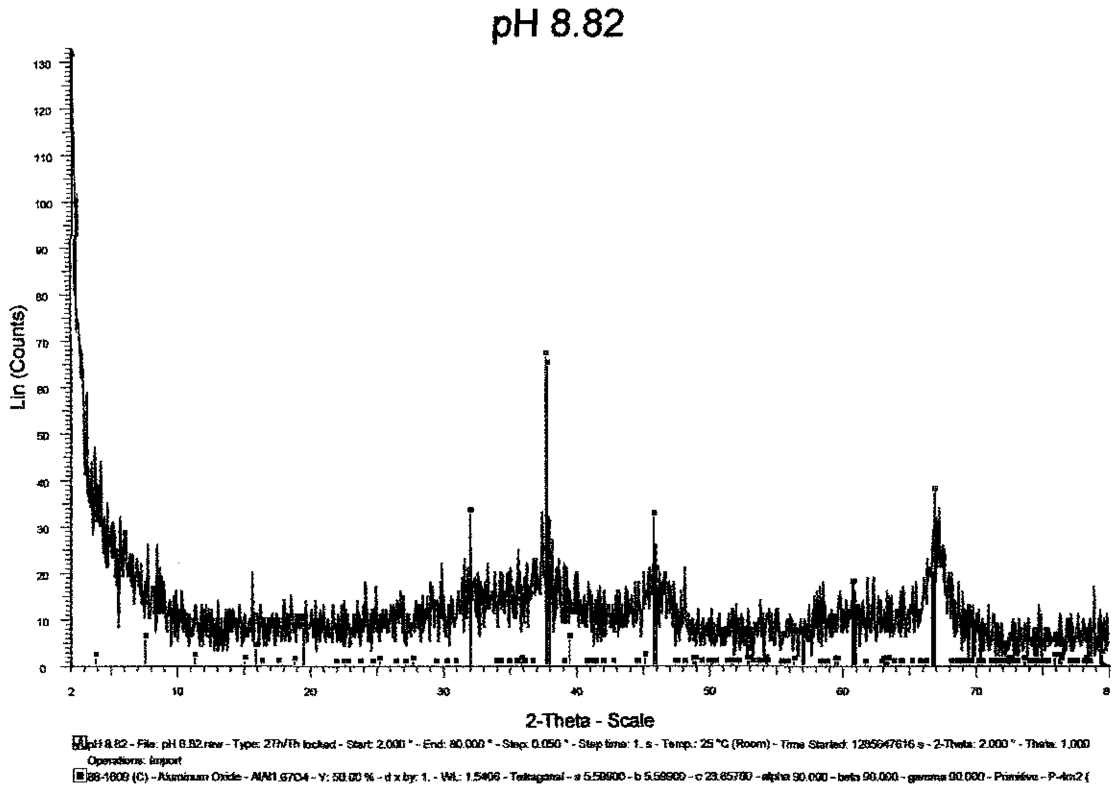


FIGURE 4: X-ray Diffraction analysis for Fe/Al_2O_3 At pH 8.82

4.1 DISCUSSION

Fe/Al$_2$O$_3$ at pH 5.21

From Table 5, it is shown that the weight loss is low at 350°C with only 0.83g and 1.1g for 400°C. The weight loss is higher for calcinations at 400°C because high temperature will reduce more impurities within the catalyst support such as iron(II) nitrate solution which was used during the impregnation. pH used for this sample is not suitable for impregnation method as the adsorption of the iron precursor is low and this will affect the efficiency of the catalyst as it reduced the contact of the iron precursor during reaction. Based on Table 6, the pH 5.21 colour tone is slightly lighter which imposed low concentration of impregnated iron precursor on the alumina oxide support. The sample also only hardened on the surface area which indicate that only the surface area has high water loss during the drying process. For the XRD Analysis shown in Figure 1, the only component that can be detected is only alumina oxide support. This is due to low concentration of the iron precursor on the alumina support and low temperature were used during the calcinations process.

Fe/Al$_2$O$_3$ at pH 6.72

From Table 5, it is shown that the weight loss is highest between the other two samples. The water loss higher as the iron precursor from the iron(III)nitrate solution were having better impregnation on the alumina support and thus reduce the concentration of iron in the solution which allows better drying process. The weight loss is the highest for calcinations at 400°C because high temperature will reduce more impurities within the catalyst support such as iron(II) nitrate solution which was used during the impregnation. pH used for this sample is suitable for impregnation method as this pH value allows the ion exchange between the alumina oxide and the iron(III)nitrate solution which will then higher the concentration of iron precursor on the alumina support. Based on Table 6, the pH 6.72 sample colour tone is darker which imposed high concentration of impregnated iron precursor on the alumina oxide support. The sample was not only hardened on the top surface area but also at the bottom of the area meaning better water loss distribution on the sample. For the XRD Analysis shown in Figure 2, the component that can be detected is only alumina oxide support and iron oxide. This is due to high concentration of the iron precursor on the alumina support but the low temperature during calcinations resulting higher impurities on the alumina support and thus resulting an unsmoothed graph.

Fe/Al_2O_3 at pH 5.21

From Table 5, it is shown that the weight loss is low at 350°C with only 0.86g and 0.92g for 400°C. The weight loss is higher for calcinations at 400°C because high temperature will reduce more impurities within the catalyst support such as iron(II) nitrate solution which was used during the impregnation. pH used for this sample is not suitable for impregnation method as the adsorption of the iron precursor is low and this will affect the efficiency of the catalyst as it reduced the contact of the iron precursor during reaction. Based on Table 6, the pH 8.82 colour tone was unwell distributed due to capillary flow of water. The water flow inside the catalyst will affect the hardness of the sample as the lower concentration of water will hardened more than the higher concentration of water. The colour tone was slightly darker than the sample of pH 5.21 as the impregnated iron is higher . inside the supportwhich imposed low concentration of impregnated iron precursor on the alumina oxide support. For the XRD Analysis shown in Figure 1, the only component that can be detected is only alumina oxide support. This is due to low concentration of the iron precursor on the alumina support and low temperature were used during the calcinations process.

CHAPTER 5

CONCLUSION

5.0 Conclusion

from the discussion above, it shows that the precursor, iron(III) was only detected at pH 6.72. It is clearly shows that the impregnation of iron to alumina support is suitable for pH 6.72.The PZC is a pH where the net surface charge of the oxide is zero. In solution, when the pH is greater than the PZC, the surface of the oxide is negatively charged and de-protonated. When the pH is less than the PZC, the surface of the oxide is positively charged and protonated. So oxides that are places in solutions with a pH greater than its PZC will absorb cations and oxides contacted with a solution with a pH less than its PZC will absorb anions. Thus, in this case, since the precursor is Iron (Fe^{3+}), so the solution made must be more than its PZC. This will allow the metal precursor to attach at the support body. In conclusion, the preparation for Fe/Al_2O_3 catalyst is better using wet impregnation method and is affected by the pH value of the impregnated solution. The adsorption of the iron precursor to the alumina support is occurred highly at pH 6.72 and thus increasing the catalyst efficiency.

5.1 Recommendation

Presently, the experiment is still ongoing due to unavailability of the equipments for analysis and also for calcinations process. Once the analysis equipment is available, the samples will be going through SEM analysis. The data from the analytical result will then be discussed for better improvement. In the future, the factors that affect the performance of the catalyst might be varied from time to time. One of the factors that might be included is the drying condition whether the catalyst will be dried in vacuum or with air. Apparently, there are possibilities that reducing the number of oxygen during drying will tend to increase the interaction between the support and the precursor. Better structure will enhance the performance of the catalyst.

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Appendices

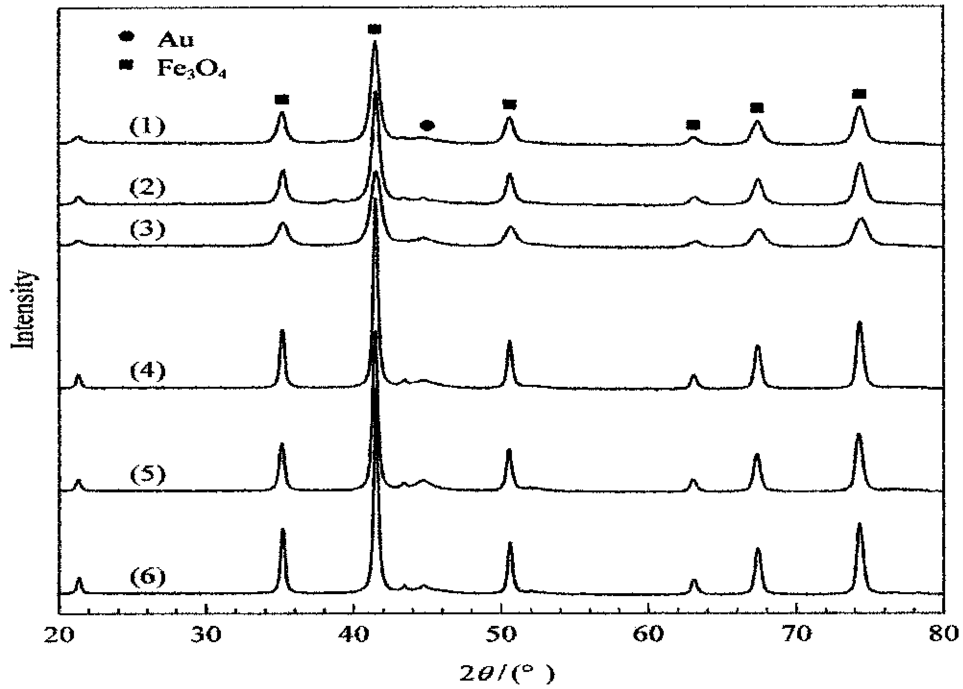

FIGURE 5: XRD patterns of Au/Fe2O3 catalysts after being reduced and WGS reaction. (1) Au/Fe2O3-CP reduced; (2) Au/Fe2O3-DP reduced;(3) Au/Fe2O3-MDP reduced; (4) Au/Fe2O3-CP used; (5) Au/Fe2O3-DP used; (6) Au/Fe2O3-MDP used.

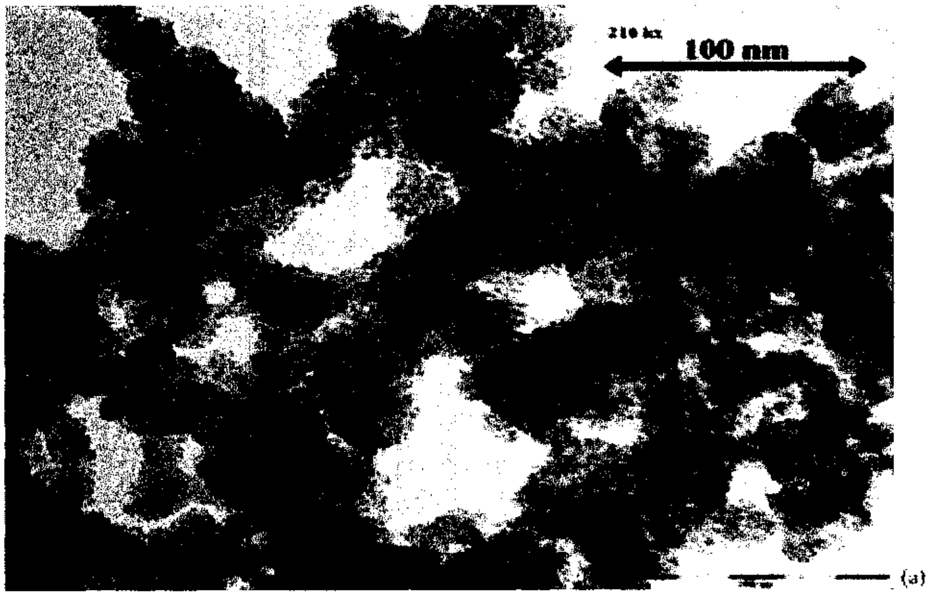

FIGURE 6: Transmission electron micrograph of iron(III) oxide deposited on silica.

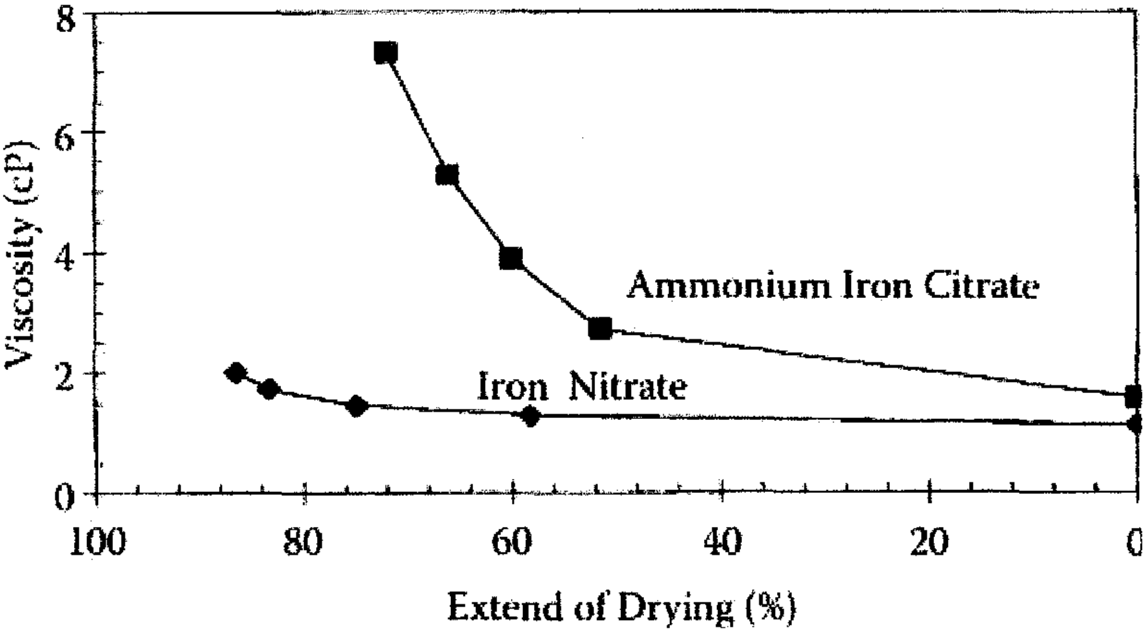

FIGURE 7: Course of viscosity during drying of solutions of ammonium iron(III) citrate and iron(III) nitrate.

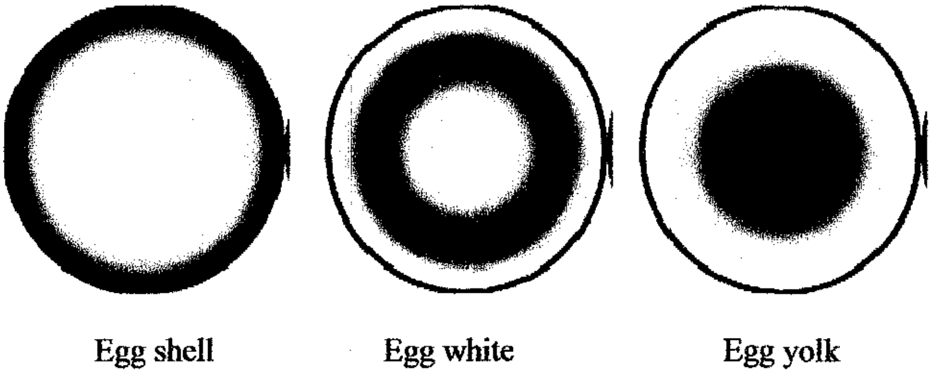

FIGURE 8: Different distribution of catalytically active component within the Support bodies.

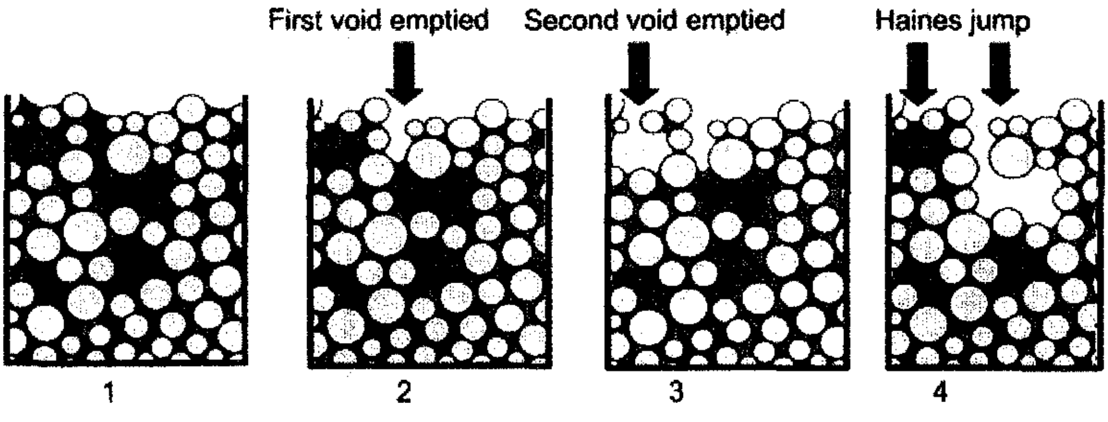

FIGURE 9: Redistribution that occurred during drying process

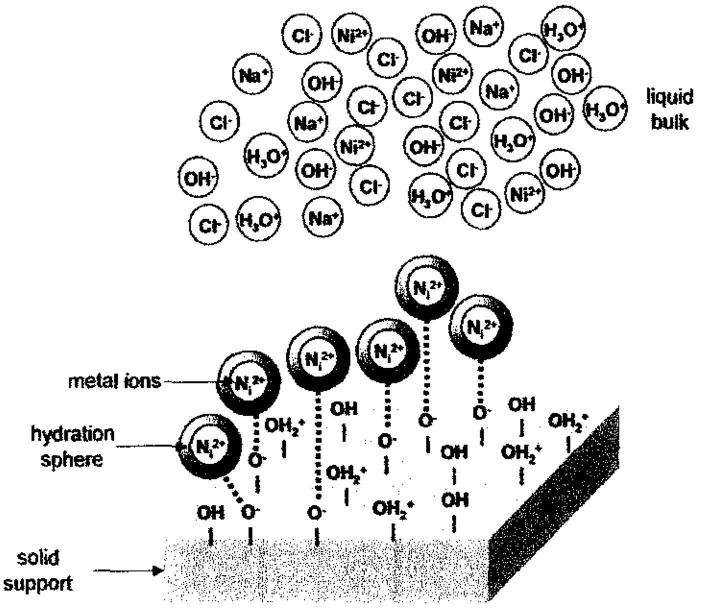

FIGURE 10: Schematic of the metal adsorption.

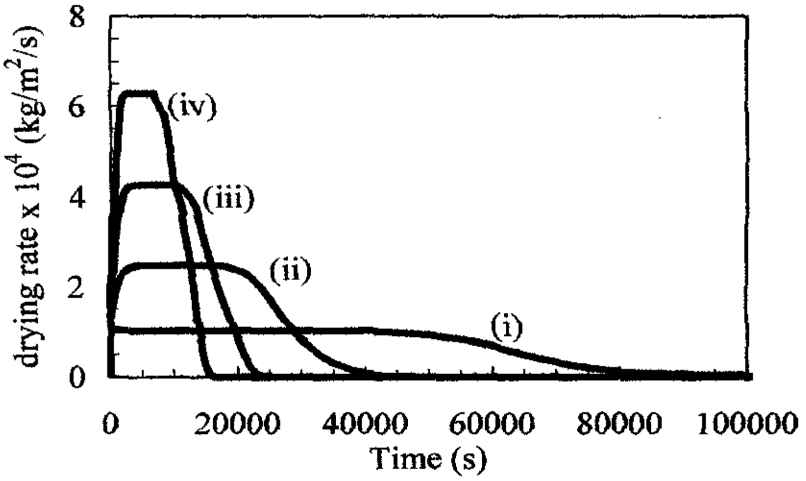

FIGURE 11: Drying rate curves at different temperature

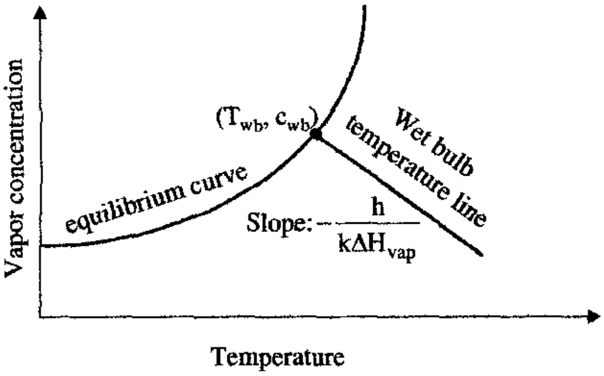

FIGURE 12: Estimation of the wet-bulb temperature.