SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

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EFFECT OF CATALYSTS ON THE FORMATION OF TITANIUM HYDRIDE UNDER HYDROGEN ATMOPSHERE

By

WONG JIA YING

Supervisor: Dr. Sheikh Abdul Rezan bin Sheikh Abdul Hamid
Co-supervisor: Dr. Sivakumar Ramakrishnan

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "**Effect of Catalysts on the Formation of Titanium Hydride Under Hydrogen Atmosphere**". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University.

Name of Student : Wong Jia Ying Signature:

Date : 25 JUNE 2018

Witness by,

Supervisor : Dr. Sheikh Abdul Rezan Bin Sheikh Abdul Hamid Signature:

Date : 25 JUNE 2018

Co-supervisor : Dr. Sivakumar Ramakrishnan Signature:

Date : 25 JUNE 2018

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LIST OF SYMBOLS

A	Reactant gas
B	Product gas
C_p	Specific heat capacity
D_{AB}	Binary diffusivity of gas A and B
e	Thermal emissivity
E_a	Activation energy
G	Gas flow rate
GoF	Goodness of fit
H	Standard Enthalpy of reaction
k	Thermal conductivity
k_p	Thermal conductivity of porous product
K_{eq}	Equilibrium constant
M_1	concentration of the concentrated solution
M_2	concentration of the dilute solution after nitric acid solution was added
M1	Molecular Weight of Species 1
M2	Molecular Weight of Species 2
n_A	Molar rate of species A
n_B	Molar rate of species B
n_C	Molar rate of species C
Nu	Nusselt Number
P_A	Partial pressure A
P_B	Partial pressure B
P_r	Partial pressure C

R	Radius
R	Correlation Factor
R’	Fractional Reaction
R	Gas constant
r_i	Inner radius of Shell i
R_{wp}	Weighed profile factor
ρ	Density
ρA	Density of Species A
ρB	Density of Species B
ρc	Density of Species C
r	Collision Diameter
Re	Reynolds number
Ro	Radius of pallet
Sc	Schmidt number
Sh	Sherwood number
Tc	Core temperature
Tg	Gas temperature
To	Initial temperature
Tp	Product temperature
Ts	Surface temperature
θ	Porosity
X_h	Degree of dehydriding
X_w	Weight different
V_1	volume of the concentrated solution

V_2	volume of the dilute solution after nitric acid solution was added
W_f	Final weight
W_i	Initial weight
λ	Wavelength
Ω	Collision integral

LIST OF ABBREVIATION

ANOVA	Analysis of Variance
BEPM	Blended Elemental Powder Metallurgy
$CaCl_2$	Calcium (II) chloride
CaF_2	Calcium fluoride
DOE	Design of Experiment
EDS	Energy Dispersive X-Ray Spectroscopy
Fe	Iron
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infra Red
H_2	Hydrogen gas
HCl	Hydrochloric acid
HF_2	Hydrogen fluoride
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
ICSD	Inorganic Crystal Structure Database
KBr	Potassium bromide
Mg	Magnesium
$MgCl_2$	Magnesium Chloride
MgH_2	Magnesium Hydride
Mg_2Ni	Magnesium Nickel
N	Nitrogen
NaOH	Sodium Hydroxide
NH_4Cl	Ammonium chloride
Ni	Nickel

O	Oxygen
P_2O_5	Pentoxide phosphorus
PPM	Particle Pellet Model
SCM	Shrinking Core Model
Ti	Titanium
$TiCl_2$	Titanium (II) chloride
$TiCl_3$	Titanium (III) chloride
$TiCl_4$	Titanium Tetrachloride
TiH_2	Titanium Hydride
TiO_2	Titanium dioxide
VRM	Volume Reaction Model

KESAN PEMANGKIN UNTUK PEMBENTUKAN TITANIUM HIDRIDA DALAM HIDROGEN ATMOSFERA

ABSTRAKS

Objektif kajian untuk penyelidikan tajuk ini adalah untuk menghasilkan titanium hidrida (TiH_2) daripada tindak balas antara magnesium hidrida (MgH_2) dan titanium tetraklorida ($TiCl_4$) dalam hidrogen atmosfera dengan penggunaan pemangkin seperti nikel (Ni), ammonium klorida (NH_4Cl) dan kalsium fluoride (CaF_2). Exsperimen ini telah dilakukan dengan menggunakan design of experiment (DOE). Parameter yang terlibat ialah suhu tindak balas (300 hingga 400 ^oC), masa tindak balas (60 hingga 120 minit) dan nisbah molar Ni to NH_4Cl (0.1 to 0.3) manakala tindak balas adalah peratusan berat badan dan tahap dehydriding. Pelbagai kaedah pencirian telah dijalankan seperti pembelauan sinar-X (XRD), mikroskop elektron pengimbas pancaran medan (SEM), spektroskopi tenaga serakan (EDS), spektoskopi Fourier transform inframerah (FTIR) dan plasma gandingan teraruh (ICP-OES). Daripada keputusan eksperimen, peratusan berat badan yang tertinggi, iaitu 17% telah dicapai dengan suhu tindak balas pada 400 ^oC selama 60 minit masa tindak balas dan nisbah molar Ni untuk NH_4Cl pada 0.5 manakala tahap dehydriding tertinggi iaitu 79.85 % diperolehi apabila suhu reaksi adalah 300 ^oC, masa reaksi adalah 120 minit dan nisbah molar Ni hingga NH_4Cl adalah 1.5. Analisis DOE menunjukkan bahawa masa tindak balas adalah parameter yang paling penting, diikuti dengan suhu tindak balas dan nisbah molar Ni untuk NH_4Cl. Kompaun yang terbentuk selepas tindak balas ialah magnesium nikel bukannya titanium hidrida kerana jumlah pemangkin nikel yang digunakan adalah besar manakala jumlah aliran gas titanium tetraklorida dalam relau adalah sedikit. Di samping itu, kewujudan reaksi terbalik dan suhu tindak balas yang tinggi telah menyebabkan desorpsi magnesium hidrida oleh nikel dalam atmosfera hidrogen dan seterusnya membentuk

magnesium nikel. Dari hasil simulasi, keadaan isoterma dan keadaan bukan isoterma model pengecutan terus (SCM) telah digunakan untuk mengkaji tindak balas. Keadaan isoterma dan keadaan bukan isoterma menunjukkan aliran yang serupa dan tahap penghampiran bererti yang berkesan dengan keputusan eksperimen selama masa reaksi 60 minit.

EFFECT OF CATALYSTS ON THE FORMATION OF TITANIUM HYDRIDE UNDER HYDROGEN ATMOPSHERE

ABSTRACT

The research objective is to produce titanium hydride (TiH_2) from the reaction between magnesium Hydride (MgH_2) and titanium tetrachloride ($TiCl_4$) under hydrogen atmosphere using catalysts such as nickel (Ni), ammonium chloride (NH_4Cl) and calcium fluoride (CaF_2). The experiment was performed by design of experiment (DOE). The parameters involved were reaction temperature (300 to 400 ^oC), reaction time (60 to 120 minutes) and molar ratio of Ni to NH_4Cl (0.1 to 0.3) while the responses were percentage of weight gain and degree of dehydriding. Various characterization method had been carried out such as X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM),Energy Dispersive X-Ray Spectroscopy (EDS), Fourier-transform infrared spectroscopy (FTIR), CHNS elemental analysis and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). From the experimental results, the high percentage of weight gain of 17 % was achieved at the reaction temperature of 400 ^oC, 60 minutes of reaction time and molar ratio of Ni to NH_4Cl of 0.5 while highest degree of dehydriding of 79.85% was obtained when reaction temperature was 300 ^oC, reaction time was 120 minutes and molar ratio of Ni to NH_4Cl was 1.5. The DOE analysis showed that reaction time was the most significant parameter, followed by reaction temperature and molar ratio of Ni to NH_4Cl. The main compound formed after the reaction was magnesium nickel instead of titanium hydride because the amount of the nickel catalyst used was large while the amount of titanium tetrachloride gas flow inside the tube furnace was too little. Besides, the existence of reverse reaction and high reaction temperature caused the desorption of magnesium hydride by nickel under hydrogen atmosphere, forming magnesium nickel. From

the simulation results, the isothermal and non-isothermal Shrinking Core Model (SCM) were used to study the reaction. Both isothermal and non-isothermal shrinking core model showed similar trend and significant closeness to the experimental result within reaction time of 60 minutes.

CHAPTER 1

INTRODUCTION

1.1 Introduction

As the ninth most abundant element in the crust of the earth and the fourth among structural metals, titanium is considered as one of the most attractive metal to mankind for more than half of a century (Fang et al., 2017). Titanium alloys have three unique properties such as high strength, low density and good corrosion resistance. This combination makes titanium very useful for many structural purposes (V. Duz, Matviychuk, Klevtsov, & Moxson, 2017). However, the growth of titanium has been restricted by the high cost and multi-step processes for both primary metal and subsequent production steps (Crowley, 2003), causing the usage of titanium is limited in aerospace industry, for corrosion protection and minor niche markets (Fray, 2008). As a result, the world production of titanium is around 50000 to 60000 tonnes/annum, which is small as compared to other metal industries such as steel and aluminium (Fray, 2008).

Normally, the titanium ingot and wrought products that produced from titanium sponge are formed by chemical reduction of titanium tetrachloride, either by Hunter process which uses pure sodium or Kroll process which uses pure magnesium (McCracken, 2010). Today, Kroll process (as shown in Figure 1.1) has dominated the titanium industry (Fang et al., 2017).

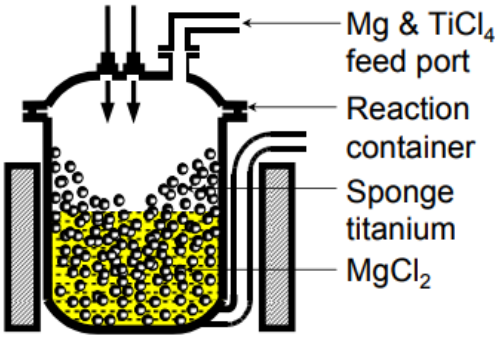

Figure 1.1: Kroll process (Isao Obana and Okabe 2006)

However, the production cost of titanium is still high. To overcome this limitation, the manufacturing of powder metallurgy titanium, namely blended elemental powder metallurgy (BEPM) method is applied. BEPM uses low cost starting blends of titanium powder and alloying powders. The relative densities of the titanium alloys manufactured by BEPM press-and-sinter method is unable to exceed 95%. As a result, titanium hydride powder rather than the conventional titanium is chosen as the starting material to increase the relative densities of the titanium alloys (V. Duz et al., 2017).Besides, titanium hydride is chosen because the cost of titanium hydride powder is lower as compared to the cost of conventional titanium sponge (Vladimir Duz, Vladimir S. Moxson, Sukhoplyuyev, & Klevtsov, 2013).A lower cost titanium hydride powder had been manufactured by ADMA Products. This process depends on the cooling sponge formed in a Kroll process with hydrogen instead of the inert gas (Froes, 2012).

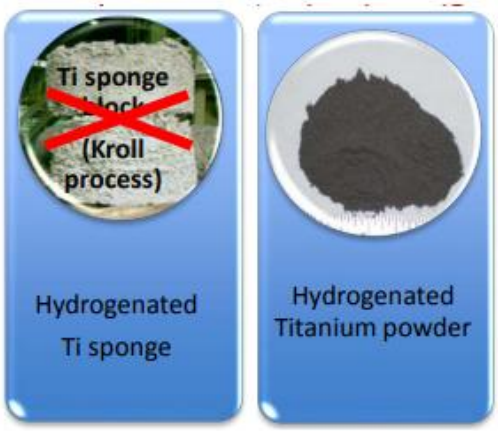

Figure 1.2 : Hydrogenated titanium sponge is replaced by lower cost hydrogenated titanium powder (Vladimir Duz et al. 2013).

The benefits of this ADMA hydrogenated titanium powder production method is listed as below (Vladimir Duz et al., 2013):

- Hydrogen can increase the magnesium utilization and decrease the reduction time.
- Time taken to remove magnesium chloride by vacuum distillation can be shorten by 80%.
- Hydrogen can completely remove the subsequent process such as the cutting, boring, shearing and crushing of the titanium sponge block (refer to Figure 1.3).
- The titanium hydride sponge mass can be ground to powder, transferred and packed under argon or vacuum condition.

Therefore, this final year project is focus on the formation of the titanium hydride from the reaction between magnesium hydride and titanium tetrachloride under hydrogen atmosphere.

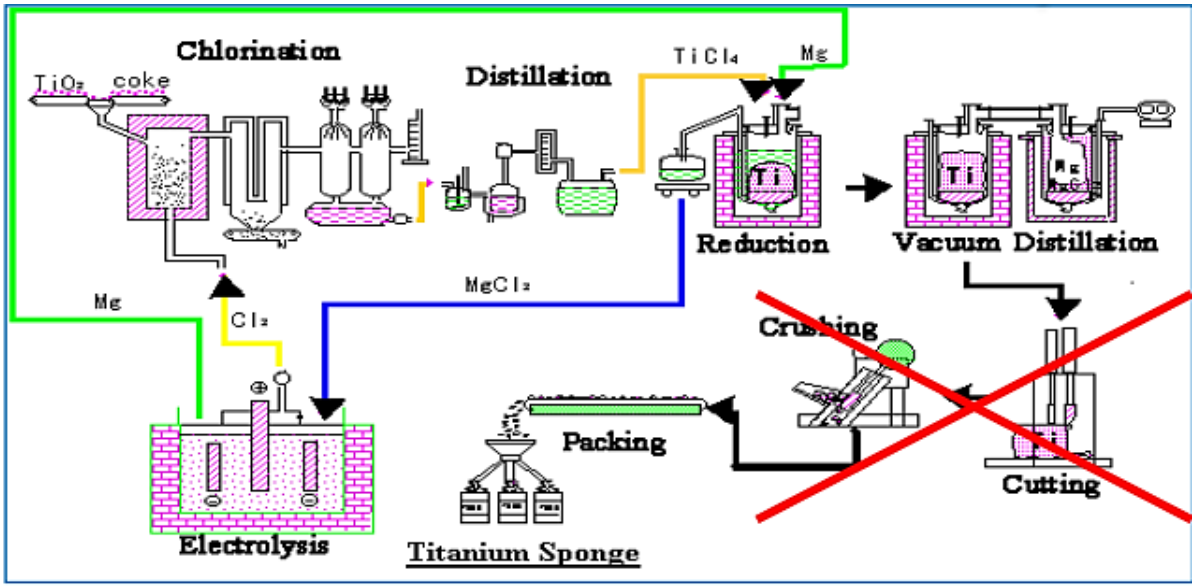

Figure 1.3: AMDA Production for Hydrogenated Titanium Powder Production (Vladimir Duz et al., 2013).

Recent years, metal hydrides are classified as hydrogen storage material and have been widely used as energy storage carriers (Yao et al., 2013). Hydrogen storage in solid hydrides has become a favorable choice because hydrogen can be stored in a safe and compact way (Ma, Wang, & Cheng, 2010). For example, magnesium hydride is light weight and low toxicity, making it safe for both human and surrounding environment. Method such as direct hydrogenation of magnesium powder can be used to synthesize magnesium hydride(Shikin, Elets, Voyt, & Gabis, 2017). Because of the high hydrogen storage capacity (7.6 wt.%), high desorption enthalpy (-74.5 kJ/mol) and low cost, magnesium is considered as a promising material for hydrogen storage (Li, Fan, Zhou, & Fang, 2016). Nevertheless, practical application of magnesium hydride is restricted due to the poor kinetics of hydrogen uptake and release as well as high thermodynamic stability (Grzech, Lafont, Magusin, & Mulder, 2012). Therefore, magnesium hydride needs higher temperature (above 673K) (Kyoi et al., 2004). Many efforts have done on the magnesium-based hydrides to decrease the desorption temperature and to speed up the re/dehydrogenation reactions. One of the

method is by using proper catalysts to enhance the kinetic of absorption/desorption (Maddah, Rajabi, & Rabiee, 2014).

Titanium tetrachloride is colorless-to-pale yellow (Merck, 1989) with penetrating odor (Merck, 1989). It exists as liquid form at room temperature and atmospheric pressure. However, it vaporizes at moderate temperatures easily (Fang et al., 2017). Titanium tetrachloride has been applied in Kroll process for magnesium reduction to produce titanium metal in sponge form (Nagesh, Rao, Ballal, & Rao, 2004). This reduction process of titanium tetrachloride by magnesium had been carried out in a molybdenum-lined crucible with the existence of argon at 1000 ^{o}C (Kroll, 1940). By using the high-purity oxygen-free titanium tetrachloride as the starting material in the reduction of Kroll process, the high-quality of titanium metal can be produced (Haiyan Zheng, Ito, & Okabe, 2007).This reduction process has been carried out in a closed reactor at high temperature under an inert gas atmosphere(Nagesh et al., 2004). This process can generate titanium metal with high purity. However, the cost of production is high due to the slow reduction process which involves an inefficient batch-type process (H. Zheng & Okabe).

In this work, the expected chemical reaction between magnesium hydride (MgH_2) and titanium tetrachloride gas ($TiCl_4$) (where ΔG°< 0 within temperature 0 ^{o}C to 100^{o}C) is shown in Equation 1.1. Catalysts such as nickel, ammonium chloride and calcium fluoride. MATLAB was used to simulate the kinetic modeling for the gas-solid reaction between the magnesium hydride and titanium tetrachloride. Shrinking Core Model is the model that was used to predict the reaction.

$2MgH_2 + TiCl_4(g) = TiH_2 + 2MgCl_2 + H_2(g)$, ΔG°(kJ/mole) = -0.0393*T -488.42 (1.1)

1.2 Problem statement

The first commercial production of titanium started in the early 1950s (Fray, 2008). Due to its fascinating properties and current cost, the reducing cost of titanium production and manufacturing has motivated the continuous research of titanium (Fang et al., 2017). However, the research of the reaction between magnesium hydride and titanium tetrachloride to produce titanium hydride is occasional. Kinetic modelling in this work can prove how fast the reaction occurs. Besides, the production cost of the titanium is high because the temperature used to reduce titanium tetrachloride using magnesium in Kroll process is about 1000 ^{o}C. Moreover, the titanium alloys that produced using conventional titanium powder have relative low densities. To overcome both high production cost and the relative low densities of titanium alloys, the lower cost of titanium hydride powder is used as starting material to replace the conventional titanium powder. Next, catalysts such as nickel, ammonium chloride and calcium fluoride are used to improve the reaction between magnesium hydride and titanium tetrachloride.

1.3 Objectives

The objectives of this work have been set and listed down as shown as below:

i) Formation of titanium hydride from the reaction of between magnesium hydride (MgH_2) and titanium tetrachloride ($TiCl_4$) using different parameters such as heating temperature, heating time and molar ratio of nickel to ammonium chloride under hydrogen gas atmosphere.

ii) Modelling the formation of titanium hydride of the reaction between $MgH_2$and $TiCl_4$ to the actual model using MATLAB software.

iii) Exploring the relationship between the processing parameters on extraction titanium hydride and the effect of catalyst on the formation of titanium hydride.

1.4 Scope of work

This research project is divided into three parts, which are the experimental work, statistical analysis and kinetics simulations.

In this first section, the magnesium powder was characterized by the X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR) for the analysis on the purity, surface morphology and identification of the sample powder with the reference spectrum library. After that, the magnesium hydride powder was ground and mixed homogeneously with the catalysts such as the nickel, ammonium chloride and calcium fluoride. Then the mixed powder was heated inside a tube furnace under different parameters and reacted with titanium tetrachloride ($TiCl_4$) vapor which hydrogen was acted as a carrier gas through the closed system. The percentage of the weight different of the sample powder before and after the reaction was calculated whereas the residual samples were characterized by XRD and SEM. The changes of the phases and the morphology of the samples were determined. Thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) analysis was done to determine thermal stability of the sample.

Next, following section is the statistical analysis part in which the Design Expert v6 software was performed to construct the matrix of the Design of Experiment, DOE. The experimental data was collected and analyzed so that the insight of the reaction between magnesium hydride and the titanium tetrachloride was studied.

The third part of this research project was to study the kinetic simulation of the reaction using MATLAB R2017b software. Shrinkage Core Model was used as the kinetic modelling and the predicted as well as the experimental reaction rate were compared and analyzed.

1.5 Outline of chapter

An outline of the project is crucial as it can ease the progress of the project and give a clear direction to the readers understand about the overview of the research. In order to give a clear outline of this final year project, the thesis of this research project was classified into different chapters.

In Chapter 1, this research project is introduced, including the brief background of study, objective, problem statement and scope of the project. Then, Chapter 2 focus on the review of the past researches that had been done. Chapter 3 explains about the method to carry out the experiment in details as well as the raw materials and the characterization methods used in this project. Next, Chapter 4 explains about the kinetic model used for the experiment. After that, all the experimental data and simulation using MATLAB R2017b software in this project arerecorded and analyzed in Chapter 5. Chapter 6concludes and summarizes the work done in this project as well as the recommendations for the future work. References that used arein another hand listed in last chapter, which is Chapter 7.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Titanium is the ninth most abundant element in the crust of the earth (Fray & Chen, 2004) and fourth among structural metals after aluminium, magnesium and iron (Fang et al., 2017).The elemental abundance of titanium is about five times less than iron and 100 times greater than copper. However, the annual use of titanium is 200 times less than copper and 2000 times less than iron for structural applications (W. Zhang, Zhu, & Cheng, 2011). Titanium has high specific strength (the ratio of strength-to-weight) which is maintained at elevated temperature, fracture resistant and the exceptional resistance to corrosion. This combination of excellent properties makes titanium and its alloys widely used in aerospace industry (refer to Figure 2.1). Besides, the usage of titanium is also increasing in other industrial and commercial applications. For examples, the refining of petroleum, chemical processing, food processing, pulp and paper, implantation of surgical, control of pollution, nuclear waste storage, cathodic protection and extractive metallurgy of electrochemical as well as marine applications (Ezugwu & Wang, 1997).

Figure 2.1: Example of titanium used in aerospace industry (Froes, 2012).

There are two main industrial routes that are applied to produce the commercial titanium, which are the Kroll and Hunter processes (Fray & Chen, 2004). Today, the Kroll process has dominated the production of titanium's industry(Fang et al., 2017) and suspended the Hunter process (Fray, 2008). These two processes are very similar. Both use highly purified titanium tetrachloride and employ a reductant element which is more reactive than titanium in order to reduce the chloride (Fray & Chen, 2004). For examples, Kroll process reduce titanium tetrachloride using magnesium while Hunter process relies on sodium to for reduction of titanium tetrachloride (Fang et al., 2017). The idea behind this method is that the oxygen is impossible to be removed directly from titanium dioxide. Therefore, the formation of chloride can help to purify and separate the oxygen content (Fray & Chen, 2004).

The major steps of the Kroll process involve the (i) chlorination process of a high-grade titanium dioxide using chlorine gas in the presence of carbon to form titanium tetrachloride, (ii) production of titanium metal by reducing of titanium tetrachloride using magnesium and (iii) the electrolysis of magnesium chloride(Kang & Okabe, 2014). The schematic figure of the production of titanium using Kroll process can refer to Figure 2.2 while the flow chart of the major steps for titanium production in Kroll Process can refer to Figure 2.3.

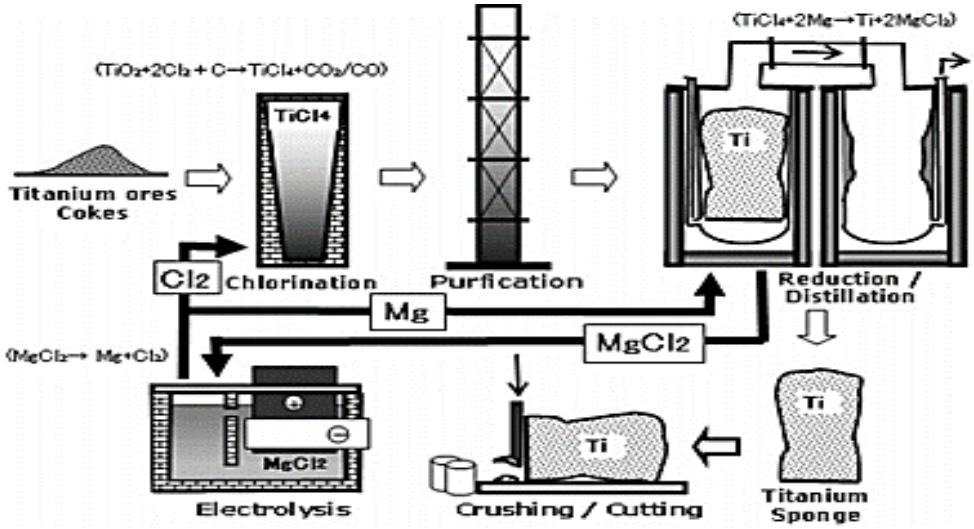

Figure 2.2 : Schematic of Kroll process (Fray, 2008).

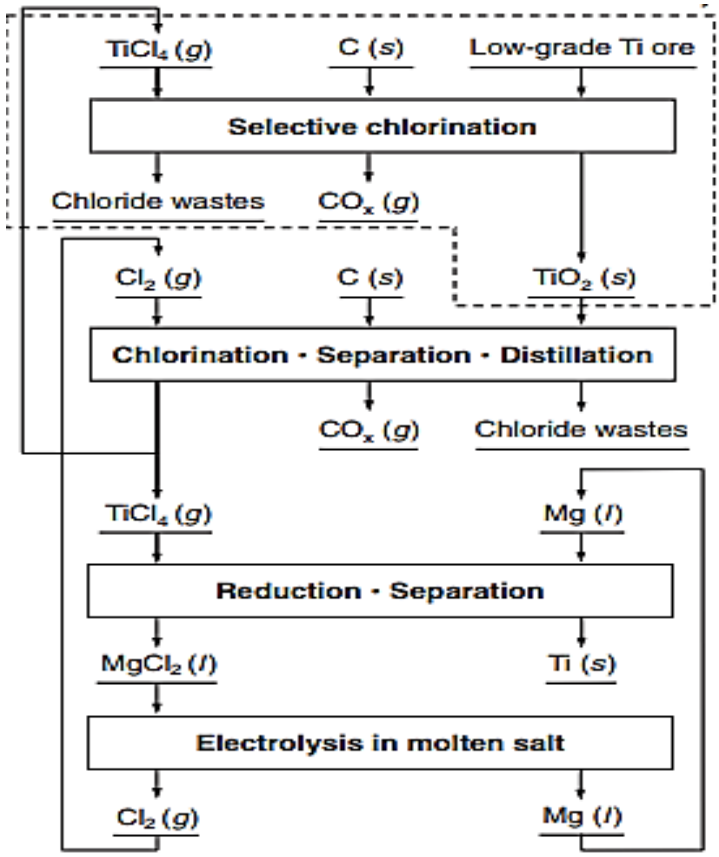

Figure 2.3 : Flow diagram of the major steps for titanium production in Kroll Process(Kang & Okabe, 2014).

The production cost of conventional titanium is high. Therefore, to produce a low cost of titanium, a powder metallurgy production of titanium namely blended elemental powder metallurgy (BEPM) is applied. This method is potentially the lowest cost production process to achieve desirable properties of produced titanium alloys because low cost titanium powder is used as starting material. However, one of the limitation of BEPM is that the relative densities of the titanium alloys that produced by BEPM press-and-sinter method is not able to exceed 95%. To increase the relative densities of the titanium alloys, a revolutionary new approach is applied. Titanium hydride powder rather than the conventional titanium is chosen as the starting material (V. Duz et al., 2017). Apart from that, cost of titanium hydride powder is used because of its lower cost as compared to the conventional titanium sponge (Vladimir Duz et al., 2013). The lower cost titanium hydride powder was manufactured by ADMA Products. The process depends on the cooling sponge formed in a Kroll process with hydrogen instead of the inert gas (Froes, 2012). The titanium hydride powder that introduced together with titanium tetrachloride affects the kinetics of the magnesium reduction process beneficially(Sanjith Udayakumar, 2017). This is because the additionally emitted atomic hydrogen can decrease oxides in the system, clean the product's interparticle interfaces and improve the diffusion between the components of powder mixture (V. A. Duz, Moxson, Abakumov, Ivasishin, & Klevtsov, 2012).

2.2 Design of Experiment (DOE)

In the 1920s and 1930s, Design of experiments (DOE) was invented by Ronald A. Fisher and he proved that valid conclusions could be made from experiments with natural fluctuations in his book on the design of experiments. The natural fluctuations are temperature, condition of soil and rain fall in the presence of nuisance parameters (Telford, 2007). DOE had been applied in three methods: traditional methods, Taguchi's methods and Shainin methods. In the 1930s, Sir Ronald Fisher used the traditional DOE method for

the problems of agricultural. Next, Dr Taguchi from Japan refined the technique. The objective of refining the techniques is to achieve the robust product designs against variation sources. Meanwhile for the Shainin method which was designed and developed by Dorian Shainin, this method used a variation of techniques to solve problems for existing products (R. Konda, 1999).

DOE is a powerful tool because it is applied to investigate the causes of process variation which had been hidden deeply (R. Konda, 1999). It is a structured and organized technique in conducting and analyzing the controlled tests so that a response variable which is influenced by the factors can be determined (Telford, 2007). DOE method is also more efficient and reliable as compared to the one-factor-at-a-time experiments where only one factor is changed at a time and all the other factors remain unchanged (Houssem R. E. H. Bouchekara, Mohamed Boucherma, & Allag, 2011). This is because DOE technique can specify certain levels of the combinations of factors when conducting individual runs in the experiment (Telford, 2007). Besides, DOE can show the ways to conduct the fewest experiments number while maintaining the most significant information. In other words, DOE can investigate the values of independent variable at which a limited experiments number will be carried out (Dong-Woo Kim, Myeong-Woo Cho, Tae-Il Seo, & Lee, 2008)

The function of factorial experimental designs is to determine the effects of different factors by varying the factors simultaneously rather than changing only one factor at one time. The sensitivity to each factor could be estimated by DOE as well as to the combined effect of two or more factors (Telford, 2007). For example, the full factorial design can explore all the possible combinations of the factors in the experiment. The full factorial designs is beneficial as the data can be made efficiently and do not mix up with the effect of

other parameters. Hence, the main and the interaction effects are possible to be evaluated clearly (Cavazzuti, 2013).

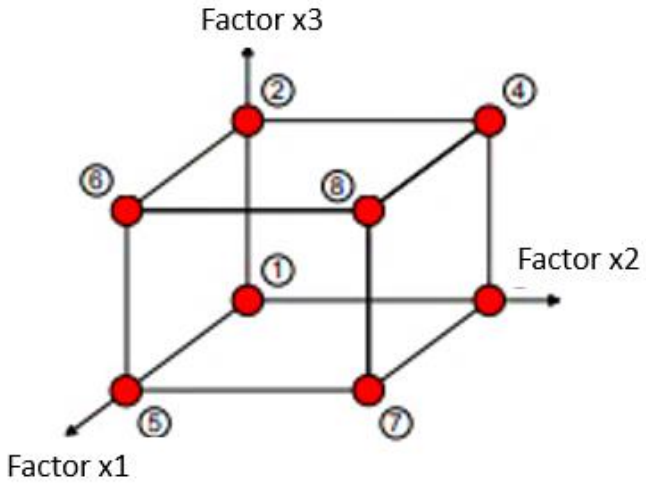

Figure 2.4: Full factorial in three dimensions (Houssem R. E. H. Bouchekara et al., 2011).

The design symbol X^k is the k factors with x level of a system in an experiment. Two levels are used for each factor at which -1 is denoted for the low level of each factor while +1 is for the high level of each factor. As that, the number of experiments that can be conducted using full factorial design with 2 levels is shown in Figure 2.4 (Houssem R. E. H. Bouchekara et al., 2011):

$$n = 2^k \quad (1.1)$$

where n is the number of experiment and k is the number of factors to be considered

DOE had been used in many field due to its effectiveness. For example, in 2008 Dong-Woo Kim et al applied DOE in a research to minimize the thrust forces in the step-feed micro drilling process. This operation greatly depended on precision of the production process. To minimize micro drilling thrust, smaller holes, greater aspect ratios and higher speed were required. However, undesirable characteristics were observed if the cutting

depth increase. Therefore, to minimize the thrust forces, three cutting parameters were chosen to be optimized based on the DOE. The three parameters were rate of feed, speed of cutting and step-feed (Dong-Woo Kim et al., 2008).

In this work, similar approach was applied to generate DOE for the experiment. There were three parameters used for this experiment, such as the heating temperature, heating time and molar ratio of nickel to ammonia chloride. For each parameter, two levels were set, which are high (+1) and low (-1). Three central points were added as the control points to control the experiment.

2.3 Formation of Titanium Hydride

In this section, the process for the formation of titanium hydride is discussed. Magnesium hydride reacts with vapor of titanium tetrachloride under the hydrogen gas atmosphere (Sanjith et.al., 2017). The main components of this reaction are magnesium hydride and titanium tetrachloride while the catalysts such as nickel, ammonia chloride and calcium fluoride are used to enhance the reaction.

2.3.1 Magnesium hydride

Metal such as magnesium is light and abundant (Ma et al., 2010). Magnesium exists 0.13 wt % in sea water and 2.76 wt % in earth crust(Crivello et al., 2016). Hydride of magnesium is a promising hydrogen storage material because of its high gravimetric hydrogen capacity (7.6 wt.%) and outstanding reversibility. However, the practical application of magnesium hydride-based hydrogen storage systems is limited by the unfavorable thermodynamics and slow kinetics for hydrogen uptake and release (Crivello et al., 2016). Due to this slow hydrogen absorption and desorption kinetics, high temperatures such as temperature above 673 K is demanded. To increase the practical use of magnesium

hydride system, these weaknesses have to be enhanced without affecting the beneficial storage properties significantly (Kyoi et al., 2004).

In recent years, many efforts have focused on magnesium hydrides to increase the re/dehydrogenation reactions and decrease the desorption temperature. By changing the microstructure of the hydride using mechanical alloying, the stability of the hydrides can be reduced. Besides, adding proper catalysts can also help to enhance the kinetic of absorption/desorption (Maddah et al., 2014). The microstructure of solid magnesium hydride is tetragonal structure with rutile type. It is specified by a lattice parameter *a* and the *c*/*a* ratio. Figure 2.6 shows the micrographs of magnesium hydride using SEM while Figure 2.6 crystal structure of magnesium hydride. At the same time, the properties of magnesium hydride are shown in Table 2.1

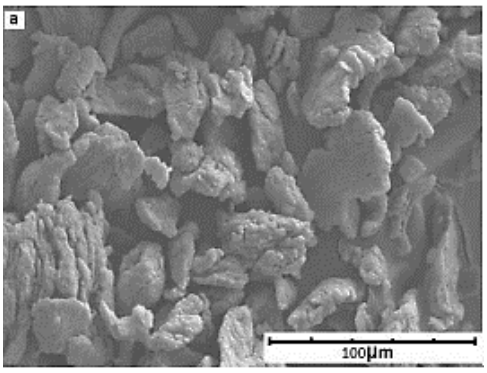

Figure 2.5 : SEM micrographs of magnesium hydride powder (Maddah, Rajabi, and Rabiee 2014).

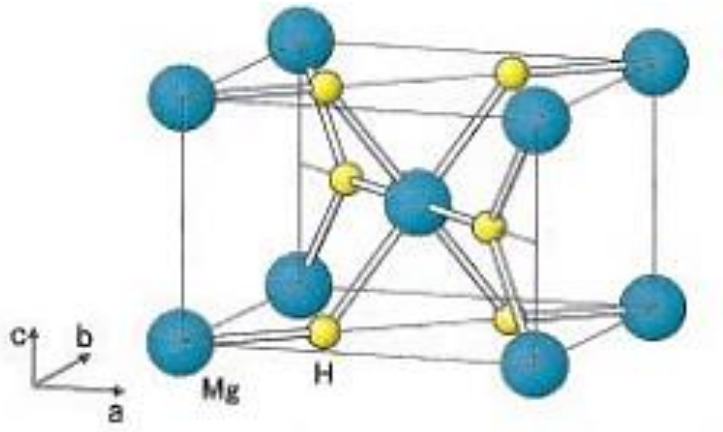

Figure 2.6 : The crystal structure of MgH_2 (Noritake et al. 2002)

Table 2.1 : Properties of Magnesium Hydride

Properties	**Value of each properties**
Molar mass	26.32 g/mol
Density	1.45 g/cm³
Specific heat capacity	35.4 J/mol K
Standard molar entropy	31.1 J/mol K
Standard enthalpy of formation	-75.2 kJ/mol K
Gibbs free energy	-35.9 kJ/mol K

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2.3.2 Titanium Hydride

The chemical compound of titanium and hydrogenis known as titanium hydride. It is a brittle powder which highly reactive when exposed to strong oxidizersor heat (Mwamba & Chown, 2011). Titanium hydride, TiH_x(x = 1, 2) can be formed because the titanium is a transition metal that can store a huge amount of hydrogen in a small volume. Subsequently, titanium and its alloys are considered as the attractive materials used in construction of

containers for hydrogen can be applied as a fuel for vehicles on the road (Duś, Nowicka, & Wolfram, 1992).

Titanium hydride is a non-stoichiometric compound. It is formed when titanium reacts with hydrogen as shown in Equation 2.2 (H. Zhang & Kisi, 1997).

$$\text{Ti (s)} + H_2\,\text{(g)} = TiH_2\,\text{(s)}\ (\Delta G°\text{(kJ/mole)} = -0.0393*T - 488.42) \quad (2.2)$$

Hydrogenation process is a process where the solid solution of titanium hydrogen is formed, followed by the formation of titanium hydride (H. Zhang & Kisi, 1997). Normally hydrogen atoms are distributed randomly along lattice sites and sited tetrahedrally with respect to titanium atoms. The transformation of phase happens replying on the content of hydrogen (Xu, Cheung, & Shi, 2007). As compared to other metal hydrides, titanium hydride is in tetragonal structure at ambient conditions with long range of temperature stability (R. Selva Vennila, A. Durygin, Marco Merlini, Zhongwu Wang, & Saxena, 2008). Titanium hydride acts as a catalyst in preparation of titanium compounds with pure hydrogen for the ceramic and glass formation which seals from a combination of titanium or titanium hydride powder form and titanium coatings. (R. Selva Vennila et al., 2008)

The bulk properties of titanium hydride has been widely studied (Duś et al., 1992). The advantage of titanium hydride is its brittleness which can help breaking down the compound into powder product. Due to this reason, titanium hydride provides a low-cost process route to make titanium alloys into useful components by powder metallurgy. The manufacturing cost of titanium product is nine times lower than the conventional method by using the powder of titanium hydride (Mwamba & Chown, 2011). Apart from that, dehydrogenation of magnesium hydride can produce titanium powder. With this, the particular titanium hydride powder can be consolidated to form fine grained titanium components. The titanium hydride can be dehydrogenated in two steps with heating

temperature up to 650 ^{o}C for 4 hours at argon gas atmosphere which shown as below: (Bhosle, Baburaj, Miranova, & Salama, 2003):

$$TiH_2 \text{ ----> } TiH_x \text{ ----> } \alpha\text{-}Ti \quad (2.3)$$

where $0.7 < x < 1.1$

Figure 2.7 shows the SEM image of the particles of titanium hydride powder which has been produced by ball milling the titanium in a hydrogen atmosphere. The image shows that the shape of the powder grains is irregular. The size of the titanium hydride ranges from 0.5 µm to 50 µm (Paulin et al., 2010).

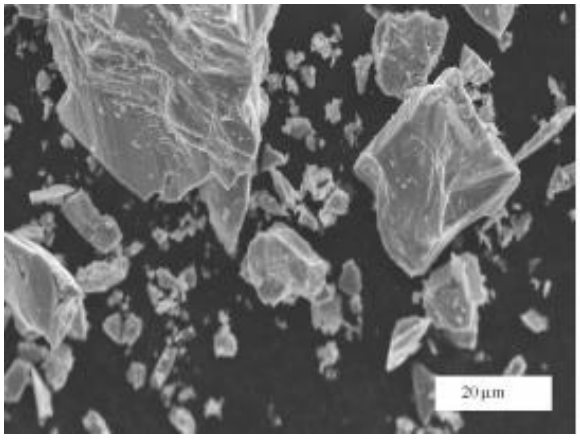

Figure 2.7: SEM image of the titanium hydride powder (Paulin et al. 2010)

2.3.3 Low Cost Production of Titanium Hydride

Powder metallurgy method is attractive in the titanium industrial because it can decrease the cost of the titanium component and at the same time enhancing their chemical and physical properties (V. A. Duz et al., 2012). Process of conventional powder metallurgy is already well developed and becomes mature in the industry. The commercial success of titanium hydride powder metallurgy method replies on the low cost but high-quality titanium hydride powder (V. Duz et al., 2017). Traditional titanium hydride is produced by the

hydrogenation process using low grade of titanium sponge (refer to Figure 2.8), turning and other titanium material due to the cost of titanium scrap is encouraging. The titanium charge is heated above 600 ^{o}C in vacuum condition to dissolve the oxide surface. The dissolution of oxide surface acts as the barriers with hydrogen and titanium charge is exposed in the hydrogen atmosphere of prescribed pressure with the temperature of 400 ^{o}C to 600 ^{o}C. The advantage of this method is that the process is relatively simple. However, vacuum condition (10^{-2} – 10^{-3} Pa) at the first stage, especially in the case of using bulky charge is needed for long exposure so that uniform distribution of hydrogen through the final product can be obtained (Qian & Froes, 2015). The hydrogenated titanium is produced based on the hydrogenated of already formed titanium materials. Hence, the cost of the hydrogenated titanium cannot be lower than that of the titanium. To accomplish the goal of low cost Blended Elemental Powder Metallurgy, the production of hydride powder should be at least cheaper than the primary titanium product (V. Duz et al., 2017).

Figure 2.8: Hydrogenated titanium sponge (V. A. Duz et al., 2012)

ADMA Product, Inc. had developed a new hydrogenation method to produce a cost-effective titanium hydride powder (Fang et al., 2017). The key feature of this new approach is the integration of the production of titanium and its hydrogenation in one continuous cycle

(Qian & Froes, 2015). The hydrogenated titanium powders are formed in the following steps. The first step is the reduction of titanium tetrachloride with magnesium and second step is the purification of titanium sponge by vacuum distillation and hydrogenation (V. A. Duz et al., 2012). The chemical reactions of titanium reduction using hydrogen is shown in equation 4 to equation 8 (V. Duz et al., 2017). The titanium sponge hydrogenation can be done in the same vessel upon the cooling from the distillation temperature after the reduction/distillation cycle(V. Duz et al., 2017; Qian & Froes, 2015). This innovation requires the magnesium thermite process to be modified, which including the equipment redesign and adjusted correlations between production of sponge and hydrogenation systems (Qian & Froes, 2015).

$$TiCl_4 + H_2\,(g) + 2Mg \rightarrow TiH_2 + 2MgCl_2\ (\Delta G^\circ = -616.95 + 0.2028T\ (kJ/mole)) \quad (2.4)$$

$$2TiCl_4\,(g) + H_2\,(g) \rightarrow 2TiCl_3\,(s) + 2HCl\,(g)\ (\Delta G^\circ = -100.62 + 0.1756T\ (kJ/mole)) \quad (2.5)$$

$$TiCl_3\,(s) + \frac{3}{2}Mg\,(l) \rightarrow Ti + \frac{3}{2}MgCl_2\ (\Delta G^\circ = -244.29 + 0.0223T\ (kJ/mole)) \quad (2.6)$$

$$2HCl\,(g) + Mg\,(g) \rightarrow MgCl_2\,(l) + H_2\,(g)\ (\Delta G^\circ = -604.84 + 0.2931T\ (kJ/mole)) \quad (2.7)$$

$$Ti + H_2\,(g) \rightarrow TiH_2\ (\Delta G^\circ = -145.26 + 0.1369T(kJ/mole)) \quad (2.8)$$

The powder production technology that applied by ADMA Product, Ins. is based on breaking up the mass of titanium sponge upon its saturation with hydrogen and subsequently the titanium hydride powder can be broken up from the sponge mass (V. A. Duz et al., 2012). The hydrogenated sponge can be crushed easier (Froes, 2015), allowing many powder-crushing and milling techniques such as ball milling, jaw crusher or jet milling to be performed (Fang et al., 2017). After crushing and classifying the titanium hydride

powder, the powder is placed back in the batch furnace for dehydrogenation to form titanium metal powder. Furthermore, the hydrogenated condition is more compacted as compared to the low hydrogen sponge that produced conventionally. The hydrogen can also be removed easily with a simple vacuum anneal and the chloride content in the hydrogenated sponge is low so that porosity can be avoided and to improve the weldability (Froes, 2015).

Figure 2.9: The ADMA titanium hydride powder (V. A. Duz et al., 2012).

The ADMA titanium hydride powder (as shown in Figure 2.9) has variety of benefits such as lower cost, lower flammability, higher oxidation resistance and lower impurity content in the sintered products. The impurity content in ADMA titanium hydride is lower as compared to the conventional ASTM B348 Grade 2 powder and it is clearly shown in Table 2.2.

Table 2.2: The chemical composition of ADMA titanium hydride powder and ASTM B348 Grade 2 powder (Qian and Froes 2015).

Material	Fraction of total mass of specified impurities (%)					
	Fe	N	C	O	H	Ti
ADMA titanium hydride powder	0.03-0.16	0.030	0.010	0.020-0.060	3.80-3.85	Balance
ASTM B348 Grade 2	0.300	0.030	0.080	0.250	0.015	Balance

2.3.4 Catalysts

In this research work, magnesium hydride is used for the reduction of titanium tetrachloride at the hydrogen atmosphere. However, the hydrogen absorption and desorption of magnesium hydride is restricted by the slow kinetic and high temperature requirements, which in turn making the application use of magnesium hydride is limited (Jia & Yao, 2017). In the past decade, many efforts such as nano-structuring, alloying and the additional of catalysts have been done in order to develop new synthesis method to solve these problems (Shahi, Bhatnagar, Pandey, Dixit, & Srivastava, 2014).Among all these methods, the additional of the high-activity catalysts is one of the possible methods to improve the reaction (Bobet, Akiba, Nakamura, & Darriet, 2000; Liang, Huot, Boily, Van Neste, & Schulz, 1999).Generally, the chemical decomposition of a compound is aimed to break the bonding network between constituent elements. The bond breaking can be determined by the overlapping of the electron between the neighboring atoms. By removing the electrons which associated with a specific bond, the bond of a compound can be broken easier. Subsequently, the kinetics and thermodynamics of the decomposition of a chemical

reaction can be enhanced (Jia & Yao, 2017). As evidence, the previous studies showed that desorption of hydrogen of the catalyst-free magnesium hydride occurred only if the temperature used is 350 ^{o}C with a rather slow kinetics. By adding small amount of catalyst such as metal and non-metal elements, oxides, fluorides, hydrides and metal-based composites, the rate of hydrogen desorption of magnesium hydride has been improved significantly (J. Zhang et al., 2017).

In order to enhance the chemical reaction of this work, catalysts such as nickel, ammonium chloride and calcium fluoride are used. Nickel is used due to its ability to facilitate the hydrogen dissociative chemisorption or recombination. As result, the hydrogen sorption rates of the hydride forming metals or alloys is promoted (J. Zhang et al., 2017). Besides, ammonium chloride is chosen because it has several beneficial properties such as environmentally benign character, commercial availability and cost effectiveness. It is also have been used as catalysts for different chemical reactions in the laboratory (Pal, 2013).Next, the calcium fluoride is used due to the presence of the fluoride in the compound. Although the research on using calcium fluoride as catalyst is still limited, titanium fluoride has been proved to improve the chemisorption of hydrogen and transport into the magnesium phase. The fluorinated surface layer formation can improve the reactivity of the hydrogen as well as to protect the material from passivation (Grzech et al., 2012). Therefore, it is suitable to be used as one of the catalysts in this experiment.

2.4 Kinetic Model

Each material has different reaction mechanism. To understand the complex nature of a reaction more completely and deeply, kinetic modelling of a simple compound inside and outside should be studied.