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MULTICOMPONENT GAS-SOLID REACTIONS: KINETIC MODELLING OF NiO/Fe$_2$O$_3$ REDUCTION IN NATURAL GAS

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled: **"Multicomponent Gas-Solid Reactions: Kinetic Modelling of NiO/Fe$_2$o$_3$ Reduction in Natural Gas".** I also declare that it has not been previously submitted for the award for any degree or diploma or other similar title of this for any examining body or university.

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LIST OF SYMBOLS

A	Reactant Gas
B	Product Gas
Cp	Specific Heat Capacity
D_{AB}	Binary Diffusivity of Gas A and B
σ	Stefan-Boltzmann Constant
ε	Thermal Emissivity
Ea	Activation Energy
G	Gas Flow Rate
H	Standard Enthalpy of Reaction
I_D	Collision Integral of Diffusion
k	Thermal Conductivity
K_{eq}	Equilibrium Constant
M_A	Molecular Weight of Component A
M_B	Molecular Weight of Component B
Nu	Nusselt Number
P_A	Partial Pressure of A
P_B	Partial Pressure of B
Pr	Prandtl Number
R	Gas Constant
R_{wp}	Weighted Profile Factor
ρ	Density
ρ_A	Density of Species A
ρ_B	Density of Species B

ρ_c	Density of Species C
n_A	Molar Rate Transport for Component A
n_B	Molar Rate Transport for Component B
n_C	Molar Rate Transport for Component C
r_{AB}	Collision Diameter
r_i	Position of Reaction Interface
Re	Reynold Number
R_o	Radius of Pallet
q_{conv}	Convective Heat Transfer
q_{sens}	Sensible Heat Transport
q_{rad}	Radiation Heat Transfer Coefficient
Sc	Schmidt Number
Sh	Sherwood Number
T_o	Initial Temperature
$T_{(c)}$	Core Temperature
$T_{(g)}$	Gas Temperature
$T_{(p)}$	Product Temperature
$T_{(s)}$	Surface Temperature
e_p	Porosity of Product
e_r	Porosity of Reactant
X_R	Extent of Reduction
X_o	Percentage of Weight Reduction
W_i	Initial Weight
W_f	Final Weight
μ	Viscosity

LIST OF ABBREVIATIONS

ANOVA	Analysis of Variance
N_2	Nitrogen
C	Carbon
CHNS	Carbon Hydrogen Nitrogen Sulphur
CMC	Carboxy methyl Cellulose
CO	Carbon Monoxide
Fe	Iron
Fe_2O_3	Hematite
DOE	Design of Experiments
ICSD	Inorganic Crystal Structure Database
Ni	Nickel
NiO	Nickel Oxide
SCM	Shrinking Core Model
SEM	Scanning Electron Microscope
TGA	Thermogravimetric Analysis
XRD	X-Ray Diffraction

REAKSI MULTIKOMPONEN GAS-PEPEJAL: PEMODELAN KINETIK BAGI PENURUNAN NIKEL OKSIDA/Fe(III) OKSIDA DENGAN MENGGUNAKAN GAS ASLI

ABSTRAK

Reaksi multikomponen gas-pepejal adalah salah satu reaksi kompleks yang melibatkan dua jenis reaktan pepejal bersama dengan ejen penurunan yang dalam keadaan pepejal. Penurunan untuk multikomponen logam oksida perlu melibatkan pembakaran di suhu yang tinggi. Jadi, adalah jai satu perkara yang penting untuk menyiasat cara penyelesaian yang terbaik bagi menurunkan pengunaan kos untuk menghasilkan logam tanpa oksida. Oleh itu, dengan menggunakan metana sebagai ejen penurunan, kos untuk satu produksi dapat dikurangkan kerana harga untuk metana lebih rendah berbanding ejen penurunan yang lain dan mudah didapati. Dalam kajian ini, penurunan nikel oksida dan Fe(III) oksida dilakukan dengan menggunakan reka bentuk eksperimen (DOE) dalam perlbagai parameter. parameter yang dikaji adalah tempoh masa penurunan (1 jam ke 3 jam), suhu untuk penurunan ($800^{o}C$ ke $1000^{o}C$) dan nisbah molar NiO kepada Fe_2O_3 (0.5 ke 1.5). Model pengecutan teras bagi keadaan isoterma dan keadaan bukan isoterma telah dibentuk menggunakan perisian MATLAB. Berdasarkan model pengecutan teras, model kinetik untuk proses penurunan bolah dijalankan untuk mendapatkan tahap penurunan dan kadar tindak balas. Tahap penurunan yang diramal dan keputusan eksperimen dibandingkan. Berdasarkan analisis DOE, suhu penurunan merupakan parameter yang paling penting dalam penurunan oksida. Analisi SEM and EDX dilakukan untuk memastikan keberkesanan proses penurunan. Berdasarkan kajian, sampel yang mempunyai nisbah molar NiO kepada Fe_2O_3 iaitu 0.5, dan suhu penurunan pada $1000^{o}C$ dalam masa 3 jam menunjukkan tahap penurunan tertinggi. Berdasarkan model pengecutan teras, tahap penurunan yang diramal untuk keadaan isoterma

menunjukkan perbezaan yang besar dengan keputusan eksperimen berbanding dalam keadaan bukan isoterma.

MULTICOMPONENT GAS-SOLID REACTIONS: KINETIC MODELLING OF NiO/Fe$_3$O$_3$ REDUCTION IN NATURAL GAS

ABSTRACT

A multicomponent gas-solid reaction is one of the complex reaction that involved the two type of solid reactants with the reducing agent in the form of gas. The reduction of multi-element metal oxide requires high temperature of reduction. Thus, it is so important to discover the best solution in lowering the production cost. Therefore, by using methane as the reducing agent, the cost is reduced because of the price for methane is lower than the other reducing agents. In this study, the reduction of NiO/Fe$_2$O$_3$ by using methane is performed experimentally by using the Design of Experiment(DOE) in variation of parameters. The parameters studied are the reduction time (1hour to 3hours), reduction temperature (800°C to 1000°C) and the molar ratio of NiO to Fe$_2$O$_3$(0.5 to 1.5). Shrinking core model for the isothermal and non-isothermal condition is developed by using MATLAB programming. Based on the shrinking core model, the kinetic modelling of reduction process can be conducted in order to determine the extent of reduction and reaction rate for each condition. The predicted result and the experimental result measured is compared. Based on the DOE analysis, the reduction temperature is the most significant parameter which affect the reduction of oxide. SEM and EDX is used to determine whether the reduction is effective or not. Based on the result, the sample with 0.5 molar ratio of NiO to Fe$_2$O$_3$ which is reduced at 1000°C for 3 hours reduction time shows the highest extent of reduction. From the shrinking core model, the predicted extent of reduction for isothermal shows large different to the experimental result as compare to the non-isothermal condition.

CHAPTER 1

INTRODUCTION

1.1 Background

Mixed nickel and iron oxide materials have a potential in the wide-ranging field which commonly used in the optics, water oxidation catalysis and biomedical applications. It is possible to use in this applications due to the abundance of iron and nickel in the earth's crust. The nickel-iron metal generally can be produced from the reduction process of nickel oxide combined with the iron oxide. Despite the predicted poor solubility of iron in nickel oxide lattice which based on the equilibrium phase diagram, the general tendency of pure Fe_xO to oxidize, the single- crystal nanoparticles are nonetheless kinetically persistent even at elevated temperature which is 200^oC (Bau, Li et al. 2014)

Based on the previous studies, there are various methods that have been proposed in order to produce the nickel/iron powder but many of them are not economical (Utigard, WU et al. 2005). It is important to develop the less expensive and more effective process in the reduction of nickel/iron oxide reduction. Carbothermal reduction is one of the method that have been studied for the reduction process of metal oxides at high temperature by using carbon as the reducing agent. Based on the investigation, the carbon monoxide (CO) gas is produced (Moslim 2016).

The reduction of metal oxide is an important reaction in the field of heterogeneous catalysis and metallurgy. The common type of reducing agents that have been used was H_2, CO, CH_4 or carbon. Nickel oxide can be reduced by using hydrogen but for practical use, the hydrogen is very expensive compare to the other reducing agent such as methane. Hydrogen is frequently produced by methane reforming (Alizadeh, Jamshidi et al. 2007).

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Natural gas occurs deep beneath the earth's surface. Natural gas consists mainly of methane, a compound with one carbon atom and four hydrogen atoms. Natural gas also contains small amounts of hydrocarbon gas liquids and nonhydrocarbon gases. The use of methane could be economically beneficial and environmentally favourable.

Gas-solid reactions are frequently used in the chemical process industries which composed a broad range of operations such as combustion of solid fuels, environmental control, petroleum refinery operations and chemical production. There are two types of reactions in gas-solid reaction which is catalytic and non-catalytic reactions. Both reactions use in the wide range of applications in the Petrochemical industry.

Based on this study, the experiment is non catalytic gas-solid reactions by which the solid matrix inside the particle does not change the chemical composition with the time in the latter (Abba and Hastaoglu 1997). The reduction mechanisms that usually involved surface adsorption, activation and radical formation. The reduction kinetics are usually described using nucleation models or the shrinking core model (2005). Unreacted shrinking core model (USCM), homogeneous model, zone reaction model and grain model are the various models which have been applied to predict the conversion of a solid phase reacting with a gas. A porous solid reactant is considered to be made of small grains, and the gaseous reactant diffuses through the pores and then react with the solid(Hastaoglu and Abba 1996, 2005). The theoretical analysis of gas-solid reaction systems is very important in the engineering applications.

The kinetic modelling of nickel oxide and hematite reduction by using compressed natural gas, the multicomponent gas-solid reactions are being investigated. The reaction of this system is because of the interaction of a solid particle of the oxide with a gas stream from the compressed natural gas. The kinetic formulation of the

reaction considered the porosity of the pellet, the carbon diffusion inside the pellet and the reaction occurred during the reduction process.

In this study, three parameters are being studied by using the Design of Experiment (DOE) which are the reduction temperature, reduction time and molar ratio of NiO to Fe_2O_3. The reduction temperature for this studies is in the range of $800 - 1000^oC$ for $1 - 3$ hours of the reduction time. The kinetic mechanisms of the reduction of NiO/Fe_2O_3 at different parameters can be determine via kinetic modelling. Based on the models, the percentage of the reduction of NiO/Fe_2O_3 can be examined.

1.2 Problem Statement

This study is about the kinetic modelling of multicomponent gas-solid reaction of NiO/Fe_2O_3 by using compressed natural gas involving the multicomponent diffusion in the gas phase. The temperature for this process is the main problem by which it involved high temperature for the complete reduction process. There are various types of reducing agents that have been used in the reduction process which is H_2, CO, CH_4 or carbon. As compared to the other reducing agents, methane is a stable molecule and methane is the main component of the compressed natural gas (Rashidi, Ale Ebrahim et al. 2013). In addition, by using methane the reduction is faster in comparison with carbothermal reduction because of high carbon activity in methane (Alizadeh, Jamshidi et al. 2007).

The reduction of NiO/Fe_2O_3 have been studied by (Hastaoglu and Abba (1996)) which using the hydrogen as the reducing agent. The reactions of this reduction process have two gaseous reactants (CO_2 and H_2) and two products (CO and H_2O). The inert gas (N_2) completely purged with the pellet. Thus, there is no active gaseous reactant was

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present inside the pellet matrix. Therefore, during the reduction process, there are five gaseous components diffusing into and out of the pellet.

Based on the previous research, the reduction of multicomponent gas-solid reaction is investigated by using hydrogen as the reducing agent. The time and the temperature required for the experiment are different as compare to the methane for the reduction of single component. Thus this experiment is conducted to investigate the reactions involve for the reduction of multicomponent gas-solid reactions by using Compressed Natural Gas (CNG) which the main composition is methane as the reducing agent.

In this study, NiO powder mixed with Fe_2O_3 powder was reduced and form Ni-Fe metal at selected parameters which is reduction temperature, reduction time and molar ratio of NiO to Fe_2O_3. The parameters that influence the reduction process can be determined by the characterization of the pellet. For further studies about the reaction and the changes occured inside NiO/Fe_2O_3 pellet can be determine by using appropriate kinetic modelling. The reactions can be mathematically modelled and simulated with advance simulation programming tools and thus this will ease the future lab work.

1.3 Objectives

    i.   To study the reactions of gas-solid reactions for nickel oxide / hematite in compressed natural gas based on the reduction temperature, reduction of time and flow time for the Compressed natural gas (methane).

    ii.   To determine the optimal combination of parameters for maximum reduction by varying the different parameters namely, reduction temperature, time of reduction and molar ratio of NiO/Fe_2O_3 by using design of experiments(DOE).

iii.   To mathematically model the kinetics of nickel oxide reduction based on the effect of the above parameters.

1.4 Scope of Project

In this study, the experimental work for the reduction process were done including the statistical analysis and kinetic modelling simulation. In the experimental work, the characterization of the raw material for NiO, Fe_2O_3 and the combination of both powders are sent for characterization by X-Ray Diffraction (XRD), Scanning Electron Microscope(SEM), Fourier Transformed Infrared (FTIR) and Thermogravimetric Analysis (TGA) to determine the purity of the raw materials, sample morphology and others properties that exist. After the mixing process for both powder, the pellet is produced and the pellet undergoes the reduction process in a tube furnace. The weight loss of the sample is calculated and recorded. The further sight of the factor that influence the reaction is determined by the characterization stages. The products are sent to X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM) and CHNS Analyzer. The changes of the morphology and phases of the product will be determined.

Statistical analysis and kinetic simulation is done by using Design Expert 6.0.10 to construct the matrix of Design of Experiment (DOE) and study the equation which based on the parameters that have been used. The predicted extent of reduction and experimental results for the reduction of NiO/Fe_2O_3 are compared and analysed.

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1.5 Outline

In this thesis, the introduction and overall overview of this study is discussed in Chapter 1, which includes the problem statements, project objectives and the scope of project. Chapter 2 consists of the literature review about the reduction process which related to this study and have been done by the researches. Methodology and kinetic model with some calculations for the theoretical value is discussed in Chapter 3 and Chapter 4. The results and analysis from the experiment is discussed in Chapter 5. Last but not least, the recommendations and conclusion are highlighted in Chapter 6.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The gas-solid reactions are frequently employed in the chemical processing industries for extract on and separation processing, combustion of solid fuels, energy generation and other metallurgical processing. These reactions are classified as catalytic and non-catalytic reactions. There are some examples of non-catalytic gas-solid reactions include the coal gasification, pyrolysis and roasting of pyrites which these operations are conducted under high temperature and pressure conditions (Hastaoglu and Abba 1996). In this study, the reaction involved is non-catalytic reaction.

The mixed nickel/iron metal is used in a wide range of field in the industry. Gas-solid reactions resulting in the formation of a solid product among the most important in the metallurgical industry. By reacting the nickel oxide and hematite at a certain temperature with carbon, hydrogen or others types of reducing agents, it can be reduced to form the metallic reduced.

Natural gas occurs deep beneath the earth's surface. Natural gas consists mainly of methane, a compound with one carbon atom and four hydrogen atoms. Natural gas also contains small amounts of hydrocarbon gas liquids and nonhydrocarbon gases. The use of natural gas as a fuel and to make materials and chemicals. Natural gas is a fossil fuel which are used as a source of energy for heating, cooking and electricity generation.

The literature reviews on the kinetics and mechanism of the reduction of nickel oxide/ hematite by using the compressed natural gas (CNG) and the reduction with the others types of reducing agents and the parameters that effect the reduction of this multicomponent gas-solid reaction is discussed in this chapter.

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2.2 Reduction of Nickel Oxide / Hematite

Nickel oxide can be obtained as either a green or black crystalline powder. The mineralogical form of NiO is bunsenite. The formation of nickel oxide is the reaction between nickel powder and oxygen which is heated above 400°C. Green nickel oxide is made by heating a mixture of nickel powder and water at 1000°C. The rate of reaction can be increased by adding the NiO (Pradniak 2002). Nickel oxide has density of 6.67 g/cm^3, the melting point is 1955°C and has Mohs hardness which is 5.5. Elemental composition of nickel oxide is around 78.58% nickel and 21.42% oxide(Patnaik 2002).

The reduced metallic nickel can be produced by heating the nickel oxide with the reducing agents such as hydrogen, carbon or carbon monoxide. (Sharma, Vastola et al. 1997) has studied the reduction of nickel oxide (NiO) by using carbon as reducing agent. The rate of interaction of micron-sized of NiO with plate-like particles of the natural graphite has been studied in the temperature range between 900-1000°C in two different systems which is in closed system and free from the surrounding environment. On comparing to both of the systems, the reduction rate is more rapid in a closed system. The reduction of NiO in closed system is described by first order plots with increasing in the rate constant values with temperature. The activation energy for the reduction reaction is 75 kcal mol^{-1} higher than the activation energy for the carbon diffusion into the nickel which is about 33kcal mol^{-1}(Sharma, Vastola et al. 1997).

Hematite (Fe$_2$O$_3$) is an oxide compound which iron oxide is the main source of iron for the steel industry. Fe$_2$O$_3$ can be obtained in various polymorphs which has alpha and gamma phase. It has density of 5.242 g/cm^{3+} and the melting point is 1539 – 1565°C. (Palacios, Toledo et al. 2015) studied the hematite reduction by using methane as the reducing agent in a partial oxidation in a porous media.

(Ostrovski and Zhang 2005) had studied the reduction of iron ore by using hydrogen. Based on the experiment, the iron ore was reduced by hydrogen in the temperature range 600-925°C. One of the parameters that have been used is the effect of the gas flow rate in which the value of the gas flow rate is varied in the range of 0.5 to 1.3 L/min. The reduction gas contained 25vol% H_2 and 75vol% of Ar. The formation of the cementite is slow at the temperature 600°C as compared to the high temperature. Increasing the temperature will increase the reaction rate of the reactions.

The production of iron (Fe) from magnetite (Fe_2O_3) can be produced by undergo the reduction with methane gas. (Steinfeld; and P.Khun. 1993) has examined the system of $Fe_3O_4 + 4CH_4$ at 1 atm and the temperature above 1300K, the chemical components consist of metallic iron in the solid phase and a mixture of 66.7% H_2 and 33.3% CO in the gaseous phase. The total energy required to effect the highly endothermic transformation is about 1000kJ/mole of Fe_3O_4 reduced.

(Manukyan, Avetisyan et al. 2015) had studied the kinetic and the structural transformation of the reduction reactions. The reduction of the NiO by hydrogen and the structural transformation was studied in the temperature range of 543-1593K. Based on their study, at a lower temperature (543-773K), the reduction reaction is not complete in the product with the complex porous networked structure due to low nucleation rate and slow diffusion of water molecule outward from the sample. As compared to the high temperature reaction which above 1173K, the nucleation of Ni is spontaneous on the NiO crystal surface is due to the increased of the nuclei density, followed by the rapid growth of Ni phase.

(Hastaoglu and Abba 1996) studied the reduction of nickel oxide combined with hematite by using hydrogen. The study was investigated in the temperature range 873K-1373K. Figure2.1 shows the effect of the temperature of the bulk gas stream in the studied temperature on the conversion of the solid reactants. At a very high temperature, both NiO and Fe_2O_3 grains loosed their shapes and collapse.

a)   b)
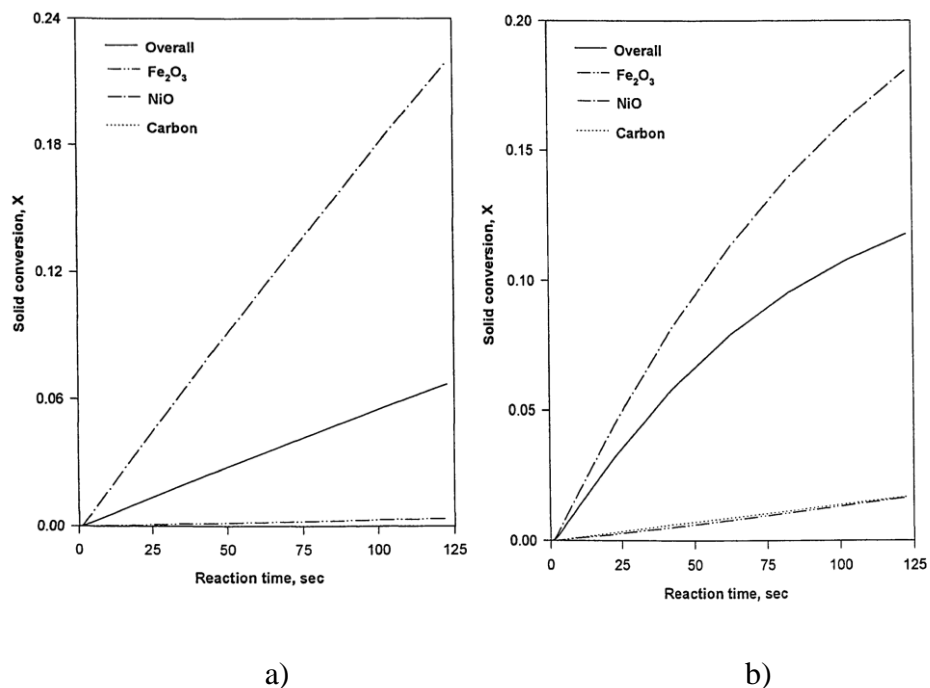
Figure 2.1: The effect of the bulk temperature on conversion at: a) T_b = 873K b) T_b=1373K and P_b = 101.3kPa(Hastaoglu and Abba 1996).

Above this temperature(1373K), the effect of the reduction is negative which lead to the reduced of conversions. A dramatic behaviour in the conversion trend is observed typically at 1373K. The overall conversion of about 9% is attained after 100 seconds reaction which is much smaller than the conversion attained at a lower temperature of 1173K (15%) for the same reaction time. Thus in this study, the temperature range that have been used in between 900-1000°C by which the effect of the reduction can be seen.

The carbon conversion is increased with increasing the reduction temperature. The study of the effect of bulk gas temperature helps to identify the suitable temperature value for the reduction reaction.

2.2.1 Reducing agent

Multicomponent gas-solid reaction involved two type of metal oxide which undergo the reduction process. There are various types of reducing agent that have been used for the previous studies. (Abba and Hastaoglu, 1997) based on their investigation, they used hydrogen as the reducing agent for the reduction of nickel oxide and hematite. The overall stoichiometry of multiple reaction is represented as:

$$NiO(s) + H_2(g) \rightarrow Ni(s) + H_2O(g) \qquad \text{(Equation 2.1)}$$

$$Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(g) \qquad \text{(Equation 2.2)}$$
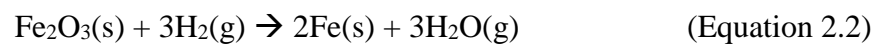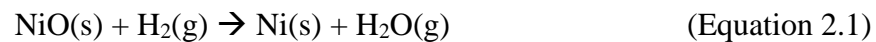
Hydrogen (H_2) has been proposed as a method for the transformation of oxide to metal in which H_2 serves as one of the main global energy carriers(Lindsey Weger, Alberto Abanades et al. 2017).

Methane-containing gas with high carbon activity has provided the strongly reducing conditions which means that the metal oxides can be reduced and carburized to metal carbides. In the process of methane cracking, the CH_4 is separated under the high temperature in the absence of oxygen in order to produce the elemental carbon and H_2. The reaction itself will generates zero emissions of CO_2(Lindsey Weger, Alberto Abanades et al. 2017). During the methane cracking process, the unreacted CH_4 is separated from H_2, and recirculated to the reactor. The hydrocarbons present are cracked in the same way as CH_4 by the thermal splitting of the C-H bonds. In addition, the

production of H_2 by the methane cracking is free of CO and CO_2 which this is due to the absence of the oxygen. In this study, the reduction process is taking place in the closed system which the inert gas, nitrogen (N_2) has been purged during the process to avoid the interruption of the sample in the presence of oxygen. The energy conversion efficiency for the methane cracking process is defined as the ratio between the energy output in the terms of H_2 and the energy input in terms of CH_4. CH_4 will supply the energy to overcome the reaction barrier ($\Delta H° = 74.85$ kJ/mol).

The reduction reactions with methane-containing gas are accompanied by the methane decomposition to solid carbon. It has been concluded by (Read PJ, Reeve DA et al. 1974) that the role of methane in the reduction reactions is to supply carbon in which it acts as the reductant. The carbon deposition will bring down the carbon activity to unity, in addition, deposited carbon blocks access of the reducing gas to the interior of oxide particles with a detrimental effect on the reduction processes.

2.2.2 Effect of reduction temperature

There are various types of reactive materials that very important and useful in the industrial. Each of the materials have their own decomposition temperature. Table 2.1 shows the decomposition temperature for various types of the reactive materials.

Table 2.1: Decomposition temperature of various reactive materials (Tiernan;, Barnes; et al. 2001)

Reactive materials	Decomposition temperature range (°C)
$Mn(NO_3)_2$	220～250
$Co(NO_3)_2$	250～280
$Ni(NO_3)_2$	Around 310
$MnCO_3$	Around 300
$CoCO_3$	220～360
$NiCO_3$	300～320
$Mn(CH_3COO)_2$	320～370
$Co(CH_3COO)_2$	Around 350
$Ni(CH_3COO)_2$	350～380
Mn_3O_4	950～1000
Co_3O_4	950～1000
NiO	950～1000
Fe_2O_3	Above 600

Based on (Alizadeh, Jamshidi and Ale Ebrahim, 2007) the reduction of nickel oxide by methane has been studied and the experiments were conducted at different temperature by using the methane-helium gas mixture which containing 20 vol-% of methane.
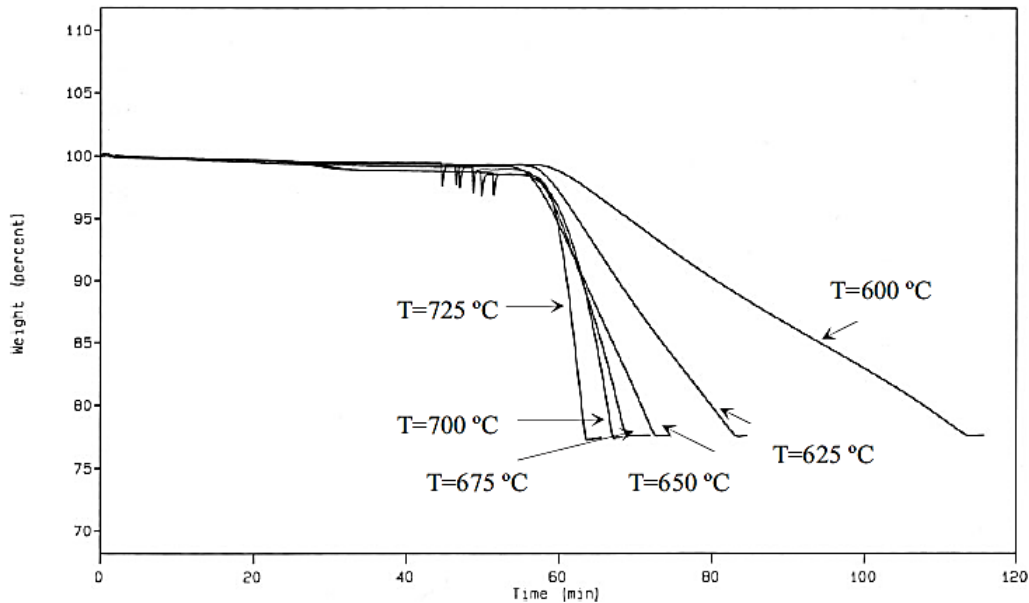
Figure 2.2: The percentages of weight changes versus time during nickel oxide

reduction at different temperatures (Alizadeh, Jamshidi and Ale Ebrahim, 2007)

The thermogravimetric curves show the induction time decrease from 13 min at

600°C to 5 min at 725°C. The complete reduction of nickel oxide by methane was

achieved at 600°C and 725°C in 68 min and 11 min as reported in (Alizadeh, Jamshidi

and Ale Ebrahim, 2007) which is shorter compared to the reduction time required by

carbon. The activation energy for the reduction of nickel oxide by carbon was found to

be 75 kcal/g mol in the temperature between 900-1000 °C which means the activation

energy is higher compare to the reduction by using the methane as the reducing agent.

Based on the previous studies, the activation energy of the reduction of Fe_2O_3 to Fe in

methane is 52.7 kcal/g mol in the temperature range of 875-950°C. Nickel oxide was

successfully reduced in the temperature range of 600-725 °C and the reduction time also

decreased. The activation energy for the reduction of nickel was found to be 63.9kcal/g

mol which is 11 kcal/g mol smaller than the reduction by carbon.

By referring the periodic table, we can see that the cobalt (Co) position is near to iron metal. Thus, we can say that the temperature for the reduction reaction of iron oxide is similar or near to the temperature for the reduction of cobalt oxide (CoO). The experiment has been studied by (Khoshandam, Jamshidi and Kumar, 2004) was carried out on the CoO pellets at atmospheric pressure in the temperature range of 800-950°C.

2.2.3 Effect of reduction time

A complete reduction of the nickel oxide by using methane was achieved at 600°C and 725°C in 68 minutes and 11 minutes which the time for the reduction is shorter than the time required for the reduction by carbon(Alizadeh, Jamshidi et al. 2007).
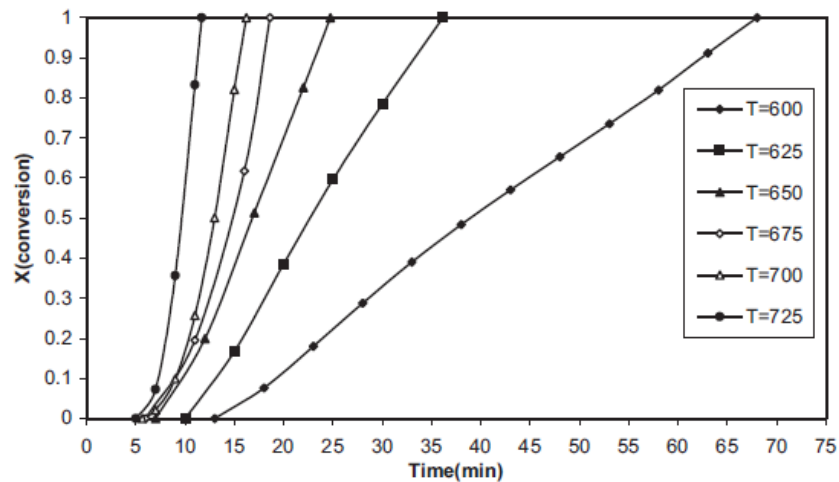
Figure 2.3: The isothermal reduction curves at different temperatures for the reduction of NiO (Alizadeh, Jamshidi et al. 2007).

From the Figure 2.3 above, it can be seen that the conversion of nickel oxide by using methane as the reductant is possible. At low temperature, the time taken for the conversion take 65 minutes to complete the conversion, compared to high temperature, the time taken is much lower which is around 11 minutes for 600°C. Based on the

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study,(Alizadeh, Jamshidi et al. 2007) the activation energy for the reduction of ZnO to Zn by methane in the temperature range of 840-930°C is found to be 67.09 kcal/g mol which is close to the reduction of nickel oxide.(Ghosh, Roy et al. 1986) reported that the activation energy of the reduction of Fe_2O_3 to Fe with methane is 52.7 kcal/g mol in the temperature range 800-950°C.

2.2.4 Effect of gas flow rate

Compressed natural gas is one of the reducing agent that have been used for the reduction of metal oxide. The flow rate of the gas played an important role in this reduction process. The gas flow rate can affect the diffusivity of gas into the grain structure. If the flow rate of the gas is low, the complete reduction cannot be achieved. The effect of gas flow rate on the rate of the reduction was investigated by (Ostrovski and Zhang, 2006). Iron ore reduction by CH_4-H_2-Ar gas was investigated as a function of temperature and gas composition. In the experiments, gas flow rate was maintained at 1L/min and the gas mixture which is Ar-CH_4-H_2 containing 35 vol% CH_4 and 55 vol% H_2 in the temperature range 600-925°C.

2.2.5 Effect of pellet shape and size

The properties of pellet and their microstructure are mainly dependent on the raw material that is used, chemical composition of raw material and the physiochemical conditions. The physiochemical conditions are like the temperature and oxygen partial pressure in the study.

Shape is one of the most important factor that affect the reduction process. This is because the diffusion of the gas through the centre of the pellet depends on the surface exposed in the sample. The reaction usually taking place at the sharp interface of the pellet. The production of spherical particles in form of a pellet is called pelletizing process. As compared with the disk shape pellet and spherical pellet, the reaction occurs easily in a disk shape pellet.

(Lin 1975) studied that the pellet size has a proportionality relationship with the Thiele modulus. The effect of pellet size with overall conversion is similar to the Thiele modulus. With increasing the pellet size, the sintering intensity, thermochemical conditions and the formation of different phases vary across its cross section. The time required for the reduction process is directly proportional to the pellet size as an example the difference in pellet size will affects the reduction process resulting in different phases and microstructures(Umadevi, Kumar et al. 2009). Thus in order to obtain the highest rate of the reduction, the pellet size should be reduced as much as possible to get the complete reduction in a short time.
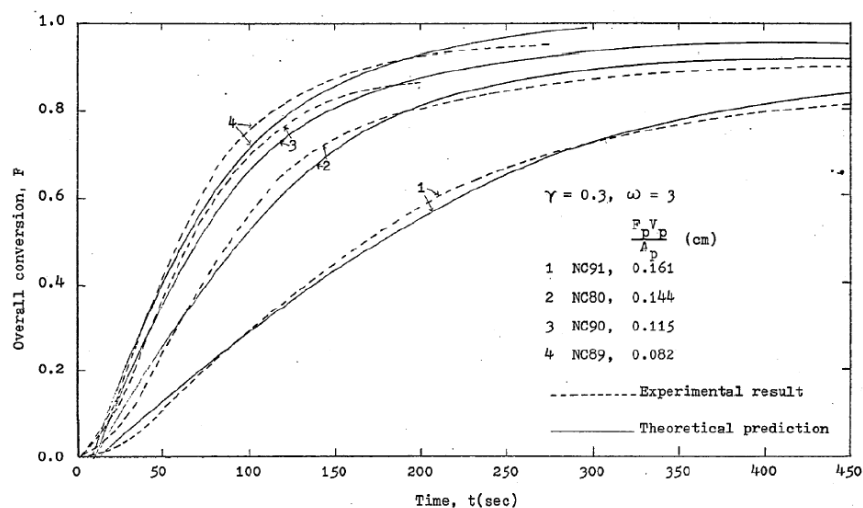

Figure 2.4: Effect of the pellet size on the overall conversion as a function of time (Lin 1975).

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2.3 Chemical Kinetics

Chemical kinetics is the study and investigation of chemical reaction which react with respect to the reaction rates, effect of various variables, re-arrangement of atoms etc. (Mondal K, Lorethova H et al. 2004) has proposed a kinetic model by using CO and H_2 as the reducing agent. The kinetics were derived based on the Arrhenius equation as shown in Equation 2.3. The study of rate of chemical reactions is called chemical kinetics in which the rate has been develop in order to determine how quickly a reaction will occur under a given circumstance. It is profitable to enhance the reaction rate of desired chemical reactions and to retard the rate of undesired reactions.

$$k = Ae^{\frac{-E_A}{RT}}$$ (Equation 2.3)

Where,

k = The rate coefficient

A = Constant

E_a = The activation energy

R = The gas constant (8.314×10^{-3} kJ mol^{-1} K^{-1})

The kinetic model for gas-solid heterogeneous reactions describes the process at the interface between two phases. The kinetic reactions can be observed by the formation of model. The reaction involves the reactions at the interface as well as the transport process within the production layer. The assumption of quasi-static diffusion is used for the standard unreacted shrinking core model. This process results in a steady-state concentration profile of gas reactant in the product layer. The general solution is very important and can be obtained for reaction kinetic including the reaction front velocity and the conversion of volume fraction of reacted solid(Xu, Sun et al. 2012).

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2.3.1 Homogeneous/ Heterogeneous Gas- Solid Reaction

Chemical reactions can be devided into homogeneous and heterogeneous reactions. The single phase involve in the reaction is called as homogeneous reactions, while for the heterogeneous reaction, it involved the reaction between two or more phases either the reaction type can be catalysed or uncatalysed.

Heterogeneous reaction occurs at contact between phases, the multicomponent gas-solid reactions involve two phase which is gas and solid. Two phases can come in contact only at a surface. Any theoretical treatment of a heterogeneous reactions must consider the properties of the boundary separating the two phase and it is important to taking in account the changes which occurred to this boundary during the course of the reaction(Gower 1971).

A general type of heterogeneous reaction can be represented by

$$aA(g) + bB(s) \;\rightarrow\; cC(g) + dD(s)$$
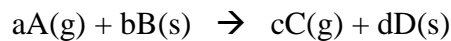
where A and C are gaseous and B and D are solid components. Some important types of single gas-solid reaction are the following(Doraiswamy, et al. 1987):

i)   Reduction and roasting of ores:

Fluid and solid reactants → Fluid and solid products

ii)   Decomposition reactions:

Solid reactants → Fluid and solid products

iii)   Oxidation and chlorination of ores:

Fluid and solid reactants → Fluid products

iv)   Gasification reactions:

Solid reactants → Fluid products

According to (Gower 1971), the interfacial reaction between the gas and solid can be divided into six types as follow:

i) Adsorption

ii) $Solid + Gas_1 = Gas_2$

iii) $Gas_1 = Solid + Gas_2$

iv) $Solid_1 + Gas = Solid_2$

v) $Solid_1 + Solid_2 = Gas$

vi) $Solid_1 + Gas_1 = Solid_2 + Gas_2$

In this study, the reaction 6 are involve in which the reaction involve are represented by the Equation 2.4.

$$NiO(s) + Fe_2O_3(s) + 4CH_4(g) \rightarrow Ni(s) + 2Fe(s) + 4CO(g) + 8H_2(g) \quad \text{(Equation 2.4)}$$
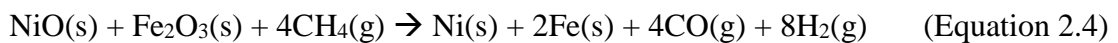
Adsorption occurs when a solid surface come in contact with a gas and it can be strongly affected by the reactivity of a solid surface. The difficulty arises from the complexity of the heterogeneous system involved. There a general reaction of gas-solid reaction must be proceed by the following sequences (Gower 1971):

i. Transport of the gaseous reactant from the bulk gas stream going through the stagnant gas layer surrounding the particle to the solid-gas interface.

ii. Transport of gaseous reactant from the solid-gas interface going through the solid product to the reactant-product interface.

iii. Reaction at the reactant-product interface to form solid and gaseous products

iv. Transport of gaseous product from the reactant-product interface through the accumulated solid product to the solid-gas interface.

v.   Transport of the gaseous product from the solid-gas interface through the stagnant gas layer surrounding the particle to the bulk gas phase.

For the exothermic or endothermic reactions, the diffusional and reaction steps will involve in convection heat transfer between the gas stream and solid surface and the conduction heat transfer within the solid reactant-product matrix (Szekely and Hastaoglu 1976). the Figure 2.5 shows the schematic diagram for the gas-solid reaction.
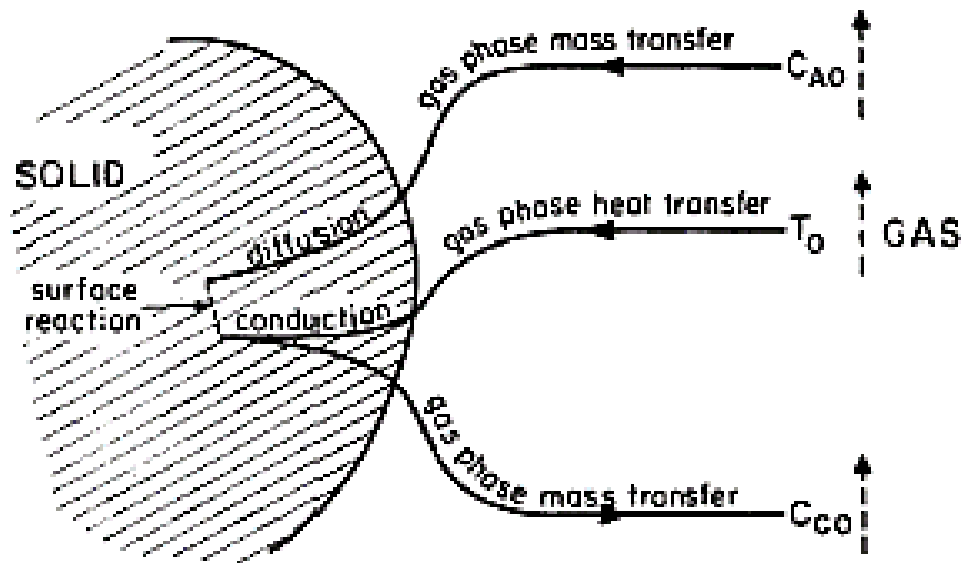
Figure 2.5: The schematic diagram for the gas-solid reaction (Szekely and Hastaoglu 1976)

2.4 Complex Reaction System

Many industrials follow the complex reaction schemes and modelling for the production of their product. The complex reaction system could be consecutive gas-solid reactions, reaction of more than one gas and solid components or reaction of more than one solid with same gas or reaction of more than one solid with the same gas. Modelling of these systems is more difficult and the model study that had been studied is shown in

Table 2.3. Table 2.2 below shows the type of the complex gas-solid reaction systems with some example.

Table 2.2: Examples of the Complex Reactions (Hastaoglu and Abba 1996)

Classification	Examples	Reference
1. Reaction of two solids with the same gas	1. Regeneration of coked catalysts 2. Reduction of a mixture of iron oxide and nickel oxide	(Ramachandran, P.A. et al. 1975) (Szekely and Hastaoglu 1976)
2. Reaction of two or more gases with the same solid	1. Reduction of iron ore with a mixture of CO and H_2 2. Decay and diffusion of gases in the subsurface	(Tsay, Q.T. et al. 1976) (Abu El Shar and Y. 1993)
3. Gaseous product of first reaction reacting with a second solid	1. Reduction of Cobalt Sulfide in the presence of CaO	(Fahim, M. A. et al. 1978)
4.Homogeneous/ Heterogeneous reaction	1. Reduction of metal chlorides with hydrogen	(Rao and K. 1981)

2.5 Model Studies

The complexity of modelling gas-solid reactions is extremely difficult to use the single model in order to incorporate all the features of these reactions. There are various types of the model that have been used to describe this reaction. The basic models which is sharp interface model volume reaction mode, pore model, the network model, particle-pellet model and miscellaneous model can be used as the basic for the modelling of gas-solid reactions.

Table 2.3: The type of model for the modelling of gas-solid reaction (Hastaoglu and

Abba 1996)

Types	Description
Sharp Interface model	This model is used for the solid reactant which has highly non-porous and the reaction occur at the sharp interface which divides the exhausted outer shell (ash layer) and the unreacted core model.
Volume Reaction Model	This model is used for the homogeneous porous solids. The rate of diffusion of the reactant gas is higher because of the high porous solid which cause by the rapid diffusion of the gas (penetrate into the solid).
Pore Model	This model involved the pore size distribution inside the solid pellet. The effect of the structural changes which is due to the diffusion of gas which lead to the pore opening and pore closure phenomena. Three product layers: 1) Product layer around each pore 2) Overlapping reaction surfaces 3) Fully development of product layer
The Network Model	This model is used to simulate the geometrical and topological properties of the structures. Based on the research, they concluded that the broader the pore size distribution of the solid, the larger the inaccessible pore volume formed in the interior. (Yortos, Y.C et al. 1984)
Particle-Pellet Model	This model referred to as the grain model. The solid consisting a number of closely packed arrangement of small non-porous particle. In addition, the grain has regular shape and uniform size that the reaction react at the sharp interface.
Miscellaneous Model	Crackling Core Model, this model is the only approximation and does not consider the basic mechanisms responsible for the sigmoidal behaviour.

2.5.1 Shrinking core model

Hydrometallurgical leaching reactions involve the non-porous solid particles by which this system can be described by the shrinking core model. The shrinking core model is used for the equation for the pore diffusion control by which it has been extended to the case of a facile heterogeneous reaction coupled to a facile homogeneous reaction which occurred within the pores of the product layer(Pritzker 1996). This model envisages the reaction to proceed topochemically at a well-defined interface which the reaction will moves inward from the outer surface of the solid particle over time. An important assumption in the use of this model is the solid reactants are considered to be highly non-porous and assumed the reaction is occurred at the sharp interface which divides the exhausted outer shell (ash layer) and the unreacted core of the solid.
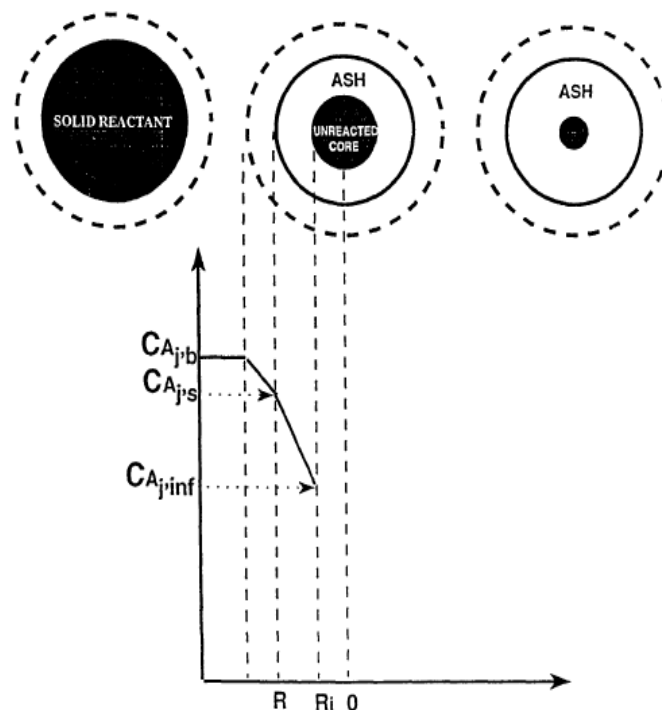

Figure 2.6: The schematic diagram represent the sharp interface model(Hastaoglu and Abba 1996)

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