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Alumina-Supported Nickel Oxide as Oxygen Carrier in a Chemical Looping Combustion of Hydrocarbon Fuel

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ABSTRACT

Chemical looping combustion has been identified as a promising combustion process with inherent capturing of carbon dioxide and electricity generation. This novel technology involves the use of solid material capable of supplying oxygen and facilitating the combustion operation in absence of nitrogen diluted air. This solid material is known as oxygen carrier. This study attempts to review the preparation and characterization of nickel- based oxygen carrier supported on alumina (NiO/Al_2O_3). Its Preparation involves evaluation or modification of support, contacting the support with impregnating solution, removal of excess solution, drying, calcination and activation. Hence, the characterizations of oxygen carrier are based on its properties (physical and chemical). The development of kinetic model to describe the reduction-oxidation reaction of active component of oxygen carrier (NiO) with hydrocarbon fuel (CH_4) and air is also put into consideration. Several assumptions are made to simplify the model. The nucleation and nuclei growth model is used to analyze the kinetic parameters contained in the model. The activation energy (E) could be determined using iso-conversion method based on the assumption that the rate of reaction at a constant extent of reaction is only a function of the temperature. Also, numerical, analytical or graphical solution of rate expression would yield kinetic constant (k).

 Keyword: characterization; chemical looping combustion; kinetics; modeling; oxygen carrier.

INTRODUCTION

Chemical looping combustion (CLC) is a new combustion process technology employed to create an exit stream that has concentrated carbon dioxide and little or no nitrogen. This technique involves the use of a metal oxide on appropriate support, which is periodically oxidized with air in the absence of fuel producing no carbon dioxide and then reduced by hydrocarbon fuel to a lower oxidation state or metal producing a concentrated carbon dioxide streams.

The basic concept of chemical looping combustion (CLC) was first employed by Lewis and Gilliland [1, 2] for the production of pure carbon dioxide. However, Ishida *et al* [3] were the first ones to use the term "chemical looping combustion" in their study. The evaluation of a chemical looping combustion power-generation system by graphic energy analysis was considered. The proposal of using CLC as a means of capturing carbon dioxide was also invented by Ishida *et al*, [4]. These authors centered their study on CO_2 recovery in a power plant with chemical looping combustion. Recently, many other related aspect of chemical looping combustion such as chemical looping reforming (CLR), chemical looping with oxygen uncoupling (CLOU), chemical looping steam reforming (SR-CLC), chemical looping hydrogen (CLH) generation and integrated gasification and chemical looping combustion (IG-CLC) have been established [5]. A

considerable amount of research work on CLC and its branches have recently been published [5-10]. Many researchers had also worked on performance analysis of combined power cycles with chemical looping combustion using gas turbines at favourble operating conditions [6, 11-14]. In a later study, coal gasification was a simpler gas turbine that operates at favourable conditions [13]. Furthermore, some authors conducted a detailed exergy analysis of these two systems [12]. Lyngfelt *et al* [15] proposed the tentative chemical looping combustion process based on an interconnected CFB and bubbling fluidized bed (BFB) for air reactor and fuel reactor respectively. Since then, more than 4000 hours of operation with several CLC demonstration units located in various countries have been reported [5]. Most of these CLC units used gaseous and solid fuels with a nominal power ranging from 300W to 3MW. More so, Partha Sarkar and Allan Chambers [16] in conjunction with Alberta Innovate-Technology futures conducted a workshop on environmental challenges and micro-Nanotechnology solutions, the workshop centered on how CO_2 could be separated from gas mixture so as to prevent greenhouse effect using chemical looping combustion technique. A chemical looping combustion system with operating principle that allows inherent CO_2 separation was considered. A CLC experiment with sour gas was employed as a case study, in the study, nickel based oxygen carrier

(VITO-40% NiO/60% NiAl$_2$O$_4$), CH$_4$ in N$_2$ balance fuel, were used as oxygen carrier (metal oxide) and fuel respectively, contacted in fluidized bed reactors.

Furthermore, Quddus [5] worked on development of a new mixed metallic oxygen carrier, Ni-Co/La-γ-Al$_2$O$_3$. Several characterization techniques to evaluate the reactivity and stability of the prepared oxygen carriers under the industrial-scale conditions of CLC processes were used. Apart from the beneficial effects of La and Co, it was found that the reducibility and structural properties of the prepared oxygen carriers influenced significantly by the different preparation methods used.

This present study is aimed at reviewing CLC technique capable of creating an exit stream that has carbon dioxide and little or no nitrogen. Nickel oxide supported on alumina and methane gas are considered as oxygen carrier and fuel respectively, contacting in two different fluidized bed reactors (reducer and oxidizer).

MATERIAL AND METHOD
Oxygen Carriers
In chemical looping combustion operation, metal/mixed metals oxide oxygen carriers that have stable performance during this operation have to be employed. Many potential oxygen carriers have been proposed, including the introduction of several supports as the inert material [5, 17-25]. The commercialization of CLC technology solely relies on the availability of appropriate and suitable oxygen carriers [5]. This has a direct impact on the amount of carrier particles to be used during CLC operation. According to Adanez *et al* [7] and Hossain *et al* [10],

the desired characteristics of a suitable oxygen carrier are identified as follows:
- Simple and low production cost.
- Minimum environmental impact.
- Excess oxygen transport capacity
- Favourable thermodynamic condition in term of complete conversion of fuel to CO$_2$ and water vapour.
- Minimum carbon formation to reduce the emission of CO$_2$ during the oxidation cycle in the air reactor (Oxidizer) and enhance the overall capture efficiency.
- Sulphur tolerant and cooking resistant.

These properties of oxygen carrier are difficult to achieve with pure metals or mineral oxides [17, 28]. Therefore, impregnated oxygen carriers are considered appropriate, because of their high surface area favoured enhanced reactivity and increased ionic conductivity [29]. In this regard, several oxygen carriers have been used and reported in the literature for CLC operation. A comprehensive detail of some of oxygen carriers had been compiled [5, 7, 10].

Table1: Summary of nickel oxide supported on different inert materials used for CLC operation.

In this study, Nickel based oxygen carrier supported on inert material is considered. Nickel oxide in combination with alumina was found to be very interesting as oxygen carrier in chemical looping combustion [12]. Ishida et al [19] tested particles of nickel oxide stabilized with NiAl2O4 for CLC. It was observed that their particles had good circulation properties, high mechanical strength, and high reactivity and also, they are highly applicable in CLC operation.

Table1: Summary of nickel oxide supported on different inert materials used for CLC operation.

Active Material(NiO)	%(wt) Composition of Active Material	Support Material	Facility Used	Kinetic Model Employed	Reference
NiO	60	YSZ	TGA	SCM	[17, 28]
NiO	58	Bentonite	TGA	SCM	[29]
NiO	60	NiAl$_2$O$_4$	TGA	SCM	[30]
NiO	60	Al$_2$O$_3$	TGA	SCM	[31]
NiO	20	Co/Al$_2$O$_4$	TPR-TPO, CREC RISER	NNGM	[32]
NiO	20	La-Al$_2$O$_4$	TPR-TPO	NNGM	[33]
NiO	40	NiAl$_2$O$_4$	TPR	SCM	[34]
NiO	15	Al$_2$O$_3$	Fixed Bed	MVM	[35]
NiO	20	Al$_2$O$_3$	CREC RISER	NNGM, SCM	[36]

Source: [5].

Preparation of Ni-Based Oxygen Carrier Supported on Alumina (NiO/Al$_2$O$_3$)
Catalyst in which the entire material constitutes it is usually made by precipitation, gel formation, or simple mixing of the component [37]. Precipitation provides a method of obtaining the solid material in a porous form. It consists of adding a precipitating agent to solutions of the desired components. Washing, drying and usually calcination and activation (or pre-treatment) are subsequent steps in the process.

The steps involved in the preparation of an oxygen carrier impregnated on a support include:
- Evaluating or modifying the support
- Contacting the support with the impregnating solution
- Removing the excess solution
- Drying
- Calcination and activation
- Metal precursor's reduction

A nickel hydrogenation oxygen carrier can be prepared on alumina by soaking the modified alumina particles with nickel

nitrate solution, draining to remove the excess solution, and heating in a furnace/oven to decompose the nitrate to nickel oxide (NiO). The final step (activation), reduction of the oxide to metallic nickel (Ni), is best carried out with the particle in place in the fluidized bed reactor by passing hydrogen through the reactor. Activation in situ prevents contamination with air and other gases which might poison the reactive Ni. In this case, no precipitation is needed.

Characterization of the Oxygen Carrier

Characterization of supported-metal oxygen carrier is based on its physical and chemical properties.

Physical Properties

The following properties are usually employed to characterize a supported oxygen carrier:

Surface Area: The standard method of measuring supported oxygen carrier or catalyst areas is based on the physical adsorption of a gas on the solid surface. According to the classical method of determining surface area, an all-glass apparatus is used to measure the volume of gas adsorbed on a sample of the solid material [37-38]. The apparatus operates at a low pressure: $0 \leq p \leq 1$ atm and the operating temperature is in the range of the normal boiling point. The gas volumes with corresponding pressures are obtained. The observed volumes in cm^3 at 0^0C and 1 atm (stp) is plotted against the pressure in mm, or as the operating temperature. Hence, the volume of one monomolecular layer of gas, V_m can be read from the curve and the surface area evaluated.

Void Volume and Solid Density: The void volume or pore volume of a catalyst or oxygen carrier particle is estimated by boiling a weighed sample immersed in water. After the air in the pores has been displaced is superficially dried and weighed. The increase in weight divided by the density of the liquid gives the volumes. Therefore, density of the solid phase ρ_s is then calculated as :

$$\rho_s = \frac{W_s}{V_s}$$

Also, the void fraction (or porosity) of the particle, ε_p, can be calculated from:

$$\varepsilon_p = \frac{v}{V_T}$$

Pore- Volume Distribution

The effectiveness of the internal surface for catalytic reactions depends not only on the volume of the void spaces, v_g, but also on the radius of the void regions. Therefore, it is desirable to know the distribution of void volume in a catalyst or oxygen carrier according to size of the pore:

There are two established methods for measuring the distribution of pore volumes:

> ➤ Mercury - penetration method
> ➤ Nitrogen – desorption method

Chemical Properties

Chemical properties of catalyst could be composition, structural behavior, acidity, reactivity and metallic phase's dispersion. In chemical looping combustion operation, reduction – oxidation reaction alters these properties. Some of

these properties may change due to enhanced metal support interactions, shape modification by agglomeration and nature of active component.

In order to establish the chemical properties, the following characterization techniques have to be employed [5].

> ➤ Temperature programmed studies for metal reactivity and crystal size.
> ➤ XPS analysis to determine metal/metal oxide phases, elemental composition and oxidation state of the active part.
> ➤ For active crystal phase, XRD analysis is require

Chemical- Looping Combustion (CLC) Process Description

The process consider here utilizes two interconnected fluidized bed reactors (oxidizer and reducer) with NiO/Al_2O_3 (Oxygen carrier) circulating between them and methane gas (fuel). These are connected and operated in a multiple cycle as shown in figure 2.2.
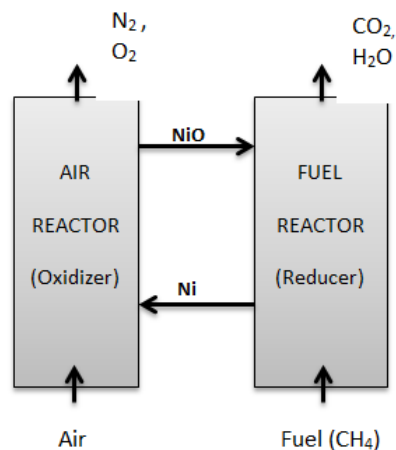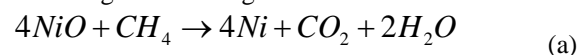

Figure 2.2: Process Description of CLC Operation.

In the fuel reactor (reducer), the methane fuel gas is oxidized completely by nickel oxide to carbon dioxide and water vapour following the overall/general reactions:

$$4NiO + CH_4 \rightarrow 4Ni + CO_2 + 2H_2O \quad \text{(a)}$$

The exit gas from the fuel reactor contains only CO_2 and H_2O, and almost pure CO_2 is obtained after water vapour (H_2O) condensation. The reduced metal oxide, Ni, is then circulated to the air reactor (oxidizer), where it is oxidized with air according to:

$$Ni + 1/2O_2 \rightarrow NiO \quad \text{(b)}$$
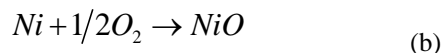
The flue gas leaving the air reactor contains N_2 and unused O_2. The total amount of heat liberates from both reduction and oxidation is equivalent to that of normal combustion, where the oxygen is in direct contact with the methane fuel gas.

Kinetic Model Formulation

The oxidation and reduction kinetics of NiO-based oxygen carrier with oxygen and methane (fuel) respectively can be modeled based on reaction mechanism and type of model employed. In this present study, nuclear and nuclei growth model (NNGM) is the type of model used to represent the kinetic of this supported oxide. NNGM incorporates the mechanism and kinetics of the gas-solid reaction without taking the morphological properties into consideration [5]. In

modeling the redox kinetic of nickel based oxygen carrier, the following assumptions are made:

- The solid (NiO) conversion and methane consumption assume first order kinetics [39-40].
- The conversion function $(f(\alpha))$ is described by reaction – rate controlling Avramin – Erofeev (A.E) linear model (n=1).
- Complete conversion of methane (fuel) to CO_2 and H_2O is assumed.
- The reaction process is also assumed to be isothermal and chemical controlling.
- Maximum solid conversion is assumed, therefore, little carbon formation during reduction cycle is observed.
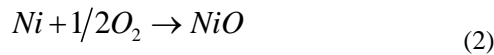
Reaction Mechanism

Based on the assumptions highlighted above, the following mechanism could be proposed for the reduction and oxidation kinetic of NiO supported on Al_2O_3 with CH_4 (fuel) and oxygen respectively:

Reduction kinetics of NiO with CH_4 (fuel) in fuel reactor:

$$4NiO + CH_4 \rightarrow 4Ni + CO_2 + 2H_2O$$
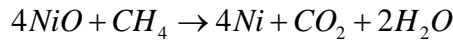
(1)

Oxidation kinetics of NiO with oxygen in air reactor:

$$Ni + 1/2O_2 \rightarrow NiO$$

(2)

The degree of reduction of NiO $f(\alpha)$ and of the composition of the methane in the gas phase is given as:

$$\frac{d\alpha(t)}{dt} = kf(\alpha)[1 - \vartheta\alpha]$$

[39-40]

(3)

The reaction rate constant (k) been a function of temperature could be expressed as:

$$k = k_o Exp[-\frac{E}{R}(\frac{1}{T} - \frac{1}{T_c})]$$

(4)

Applying A.E model $f(\alpha)$ is expressed as follows:

$$f(\alpha) = n(1-\alpha)[-In(1-\alpha)]^{\frac{n-1}{n}}$$

[40-41]

(5)

For linear model, n=1, equation 5, we have

$$\frac{d\alpha(t)}{dt} = k(1-\alpha)(1-\vartheta\alpha)$$

(6)

Combine equations 4 and 6 together, we obtain:

$$\frac{d\alpha(t)}{dt} = k_0 Exp[-\frac{E}{R}(\frac{1}{T} - \frac{1}{T_c})][1-\alpha][1-\vartheta\alpha]$$

(7)

Activation energy (E) for gas-solid reaction can be determined using iso-conversion method (Freeman 1964) based on the assumption that the rate of reaction at a constant extent of reaction, α, is only a function of the temperature:

$$(\frac{dIn(\frac{d\alpha}{dt})_\alpha}{dT_\alpha^{-1}}) = -\frac{E_\alpha}{R}$$

(8)

Integration of equation (8) yields:

$$In(\frac{d\alpha}{dt})_\alpha = -\frac{E_\alpha}{RT_\alpha} + c$$

(9)

Where c is constant of integration,

Therefore, a plot of $In(\frac{d\alpha}{dt})_\alpha$ against $\frac{1}{T_\alpha}$ will give a straight line with a slope of value E_α, which represents the activation energy for gas-solid reaction.

Subject to those highlighted assumptions, a rate expression for methane consumption in the fuel reactor can be written using equation 6 as:

$$\frac{d\alpha(t)_{CH_4}}{dt} = k_{CH_4}(1-\alpha)(1-\vartheta_{CH_4}\alpha)$$

(10)

in equation 1, stoichiometric coefficient (ϑ) of methane (CH_4) is 1, which implies, equation 10 becomes:

$$\frac{d\alpha(t)_{CH_4}}{dt} = k_{CH_4}(1-\alpha)^2$$

(11)

Re-arrangement and integration of equation (11) lead to:

$$\frac{d\alpha(t)_{CH_4}}{(1-\alpha)^2} = k_{CH_4}dt$$

(12)

For simplicity, let $\alpha(t)_{CH_4}$ be α

$$\int_{\alpha_0}^{\alpha_f} \frac{d\alpha}{(1-\alpha)^2} = \int_0^t k_{CH_4}dt$$

(13)

$$\frac{\alpha_f - \alpha_0}{(1-\alpha_f)(1-\alpha_0)} = k_{CH_4}t$$

(14)

Again, a plot of $\frac{\alpha_f - \alpha_0}{(1-\alpha_f)(1-\alpha_0)}$ against t will give a straight line with a slope of value k_{CH_4}.

CONCLUSION

The preparation, characterization and kinetics of solid material capable of supplying oxygen in a chemical looping combustion process had been reviewed. The dependence of oxygen carrier conversion on reaction time has been derived at both mathematical and kinetic levels, with the resulting rate expressions, which contain the kinetic parameters capable of describing reduction-oxidation reaction taking place in a chemical- looping combustion facility. The values of activation energy (E) and pre-exponential factor (k_0) which are significant in determination of rate constant (k) could be deduced by

iso-coversion method. Validation of the model developed with the experimental data will be the target of the next study.

Nomenclature

E activation energy, J/kmol

k reaction rate constant, s^{-1}

k_0 pre-exponential factor

n order of reaction

p pressure, atm

T temperature, K

t time, s

V_m volume of monomolecular layer

V_s volume of the solid material, m^3

V_T total volume of particle, m^3

v void volume, m^3

W_s weight of solid particle

Greek letter

ε_p void fraction or porosity

α extent of reaction

ϑ stoichiometric coefficient

ρ_s density of the solid phase, kg/m^3

Subscripts

f final value

o initial value

CH_4 methane

Abbreviation

BFB bubbling fluidized bed

CFB circulation fluidized bed

CLC chemical looping combustion

CREC RISER chemical reaction engineering center simulation

MVM modified volumetric model

NiO nickel oxide

NNGM nucleation and nuclei growth model

SCM shrinking core model

TGA thermo-gravimetric analyzer

TPO temperature programmed oxidation

TPR temperature programmed reduction

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