

Recent Advances on Preparation and Characteristics of Oxygen Carrier Particles

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Abstract – Chemical-looping combustion (CLC), characterized by high efficiency, inherent CO₂ separation and low NO_x emission, is considered as one promising CO₂ sequestration technology. The preparation of a suitable oxygen carrier for CLC is a key issue to realize the CLC technique. Recent advances on preparation and characteristics of oxygen carrier particles were reviewed in this paper. Based on a brief summary of CLC, the preparation materials and methods of oxygen carrier were introduced respectively. Finally, the physical properties of the oxygen carrier and reaction characteristics represented by the thermodynamics and kinetics were discussed. The feasibility of some materials used as oxygen carriers was evaluated through thermodynamic analysis. Three gas-solid reaction models were used to explain the reaction kinetics of the gas fuel combustion with oxygen carriers. It is a new trend to synthesis a preferable oxygen carrier using the low-cost ores and industry products instead of metal oxides and directly using the solid fuel in substitution for gas. Further, this review covers a brief introduction to the further application of CLC, especially chemical-looping hydrogen production. **Copyright © 2009 Praise Worthy Prize S.r.l. - All rights reserved.**

Keywords: Chemical Looping Combustion, Oxygen Carriers, Fluidized Beds, Preparation, Reaction Kinetics, Hydrogen Production

I. Introduction

Nowadays it has been generally acknowledged that the emission of greenhouse gases (e.g. CO₂, CH₄, and NO_x) is one of the main contributors to global warming and sea level rise, with carbon dioxide being the most prevalent of these emissions. Statistics indicated that the carbon dioxide concentration in the atmosphere has increased to 368 ppm from a preindustrial value of 280 ppm [1]. Therefore, it is significant to reduce the release of carbon dioxide emission especially after the Kyoto Protocol ratified in 1997. Bali declaration, issued at the United Nations Climate Change Conference in December 2007, also declared that it is very important to reduce the emission of greenhouse gas especially for the emission of carbon dioxide. Carbon dioxide emission is mostly due to the combustion of fossil fuels, while worldwide fossil-fuel-based power production contributes about one-third of the total CO₂ emissions annually [2]. The improvement of the conversion efficiency of the fuel and the exploration of new energy resource (e.g. the wind energy resource, solar energy resource) can reduce the release of CO₂ emission. However, the combustion of fossil fuel is still the main fuel utilization technology in the long term. Hence, a number of CO₂ sequestration technologies are currently being developed, three of which are mainly employed in fuel combustion processes. Pre-combustion, in which the fuel is de-carbonized prior to combustion, oxy-fuel combustion, which uses pure oxygen obtained from cryogenic nitrogen separation

from air and post-combustion separation, separating CO₂ from the flue gases by different approaches. In summary, the above processes turned out to be rather costly and low energy efficiency. As a result, great efforts are made to improve thermal efficiencies and reduce CO₂ sequestration cost [3]. Among all technologies, much attention is paid to chemical-looping combustion (CLC) featuring high efficiency, inherent CO₂ separation and low NO_x emission. This technique was originally proposed as a way of increasing thermal efficiency in power plants. More recently, it has been demonstrated that CLC has inherent separation advantage for CO₂ capture. CLC is regarded as a promising technology for CO₂ sequestration [4].

II. Chemical-Looping Combustion

The concept of chemical-looping combustion was firstly introduced by the German scientist Richter and Knoche in 1983[5], since then chemical-looping combustion technique has been studied widely and achieves a rapid development due to its own feature of high efficiency, inherent CO₂ separation and low NO_x emission. In summary, the study on CLC mainly focuses on three aspects: the selection and characteristics of oxygen carrier, the designing and optimization of CLC reactor and the CLC system coupled with other techniques. The chemical-looping combustion includes two stages: the oxidation stage and the reduction stage,

undertaken in the oxidation reactor and the reduction reactor respectively (Fig. 1). In the reduction reactor, the fuel (e.g. nature gas) reacts with the oxygen carrier (usually is metal oxidation), which is reduced into metal.

The outlet gas from this reactor is mostly composed of CO₂ and steam as reaction products and further separation of these two components can be carried out easily by simple condensation of steam. The free-of-water CO₂ can be sequestered or/and used for other applications. Then, the oxygen carrier found in a reduced state is transported to the oxidation reactor in which carrier regeneration with air takes place at relatively low temperatures, consequently preventing the formation of thermal NO_x. These gases can be directly released to the atmosphere with minimum environmental effects. Afterwards, the regenerated carrier is carried to the reduction reactor to reinstate a new cycle and so on for a number of repetitive cycles, while the carrier is able to withstand severe chemical and thermal stresses involved in every cycle.

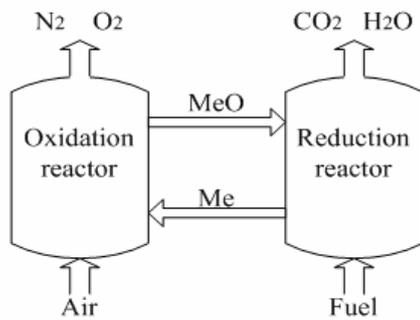
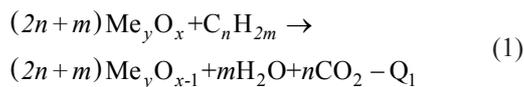


Fig. 1. Schematic diagram of chemical-looping combustion

As metal oxide particles are employed as oxygen carriers, the reaction stoichiometry in the two reactors can be written as follows:

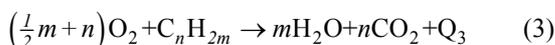
In reduction reactor:



In oxidation reactor:



The metal oxide is usually reduced to metal. The oxygen in oxidation reactor comes from the air. Generally, reaction (1) is often endothermic, while reaction (2) is exothermic with subsequent heat release. Considering the two reactors as a reactor system, the net reaction and the energy balance over reactors (1) and (2) in the process of chemical-looping combustion are as follows:



$$Q_3 = Q_2 - Q_1 \quad (4)$$

Therefore the total amount of heat evolved from reactions (1) and (2) is the same as that for normal combustion where the oxygen is in direct contact with the fuel, as illustrated in reaction (3). It should be pointed out that a full conversion from metal oxide to metal and back to metal oxide is impossible to perform in a conventional combustion system. The study on the oxygen carrier is the vital parts to research the chemical-looping combustion technique. As a successful oxygen carrier it should have the following characteristics:

- high oxygen carrier capacity;
- melting points high enough to prevent the appearance of excessive thermal sintering at the high operating temperature in all the involved processes, especially those found in the oxidation stage;
- preferable reactivity and stability in both the oxidation reactor and the reduction reactor;
- good fluidization characteristics due to run in the dual interconnected fluidized bed;
- high anti-agglomeration and mechanical stress associated with high circulation of particles;
- environmentally benign and economically feasible.

Consequently, the preparation or synthesis of an oxygen carrier with high reactivity, stable circulation performance, hardly carbon deposition and better mechanical strength is vital for the whole chemical-looping combustion system. In this paper the preparation materials, methods of a suitable oxygen carrier were summarized. The physical properties of oxygen carrier, such as the particle size, shape, density, mechanical strength and anti-agglomeration were reviewed in detail. Meanwhile, the reaction characteristics were discussed from the thermodynamics and kinetics of oxygen carrier particles in the chemical-looping combustion process.

III. The Materials for Oxygen Carrier Preparation

After the concept of chemical-looping combustion was proposed, many metal oxides, especially those from the transition metals, have been tested as potential oxygen carriers for the CLC of H₂, CH₄, which is the main component of natural gas, or water gas. The performance of oxygen carrier was relevant with the types of metal oxide, the particle size, the preparation method, the sintering temperature. Comprehensive consideration of their thermodynamic properties and physical properties, transition metal oxides such as Ni, Cu, Fe, Co, Mn are considered as the good candidates whose performances were listed in Table I. It can be found that Cu-based and Ni-based oxygen carrier particles have better performances. Initially, the bulk metal was investigated as the oxygen carrier. Good reactivity was reported [6] in the first several redox cycles. However, their reactions decreased dramatically

after many cycles mainly due to the particle agglomeration and the changes of the inter-structure or crystalline form of oxygen carriers. Apart from the activity component (metal oxides), certain inert substance should be added into the oxygen carrier as the support which can provide a high specific area and appropriate pore structure for reaction, as a binder for increasing the mechanical strength and attrition resistance, additionally, as an ion conductor enhancing the ion permeability in the solid [7]. Consequently, the inert support can improve the intensity and thermal stability of oxygen carrier. Furthermore, the inert support can decrease the oxygen carrying capacity. At present, the inert supports which have been commonly reported in the literature were SiO₂, Al₂O₃, TiO₂, ZrO₂, MgO, YSZ, montmorillonite, sepiolite, bentonite, hexavalent aluminate, and attapulgite. Different proportion of activity component and inert support can yield many kinds of oxygen carriers. As a general rule, the inert support was considered as unreact with any phase in the

reaction. However, the experimental findings have demonstrated that the inert support would react with the activity carrier to form a complex chemical compound [8]. Taking NiO/Al₂O₃ for example, the undesirable formation NiAl₂O₄ was found after reduced in the fuel reaction. De Diego [9] reported that Ni-based oxygen carriers prepared on γ -Al₂O₃ showed low reactivity and low methane combustion selectivity to CO₂ and H₂O while prepared on the support modified via thermal treatment, γ -Al₂O₃ at 1150 °C produced the phase transformation to α -Al₂O₃, or chemical deactivation with Mg or Ca oxides showed very high reactivity and selectivity.

The reasons were that NiO prepared on γ -Al₂O₃ reacted with Al₂O₃ to NiAl₂O₄ while the interaction between NiO and the support was decreased after thermal treatment or chemical deactivation. Oxygen ratios of oxygen carriers with different metal supports are summarized in Table II.

TABLE I
PERFORMANCES OF FIVE METAL OXIDES AS OXYGEN CARRIERS

Oxygen carriers	Property of Redox	Property of physical heat	Property of chemical heat	Price	Environmental benign	Remark
Fe-based	Ordinary	low	Ordinary	Low	well	Only Fe ₂ O ₃ , Fe ₃ O ₄ suitable
Cu-based	Ordinary	weak	Ordinary	Ordinary	better	Tender to sinter
Co-based	Weak	Weak	Weak	Ordinary	Ordinary	/
Mn-based	Weak	Weak	Weak	high	Ordinary	/
Ni-based	Well	Well	Well	Expensive	Low	Harmful

TABLE II
THE OXYGEN CAPACITY OF SOME OXYGEN CARRIERS

Metal oxide	oxygen capacity of pure MeO	The inert support	Mass ratio of MeO /%	oxygen capacity of oxygen carrier	complex compound	Reference
NiO	0.214	Al ₂ O ₃	20–60	0.043–0.16	NiAl ₂ O ₄	[10], [11]
		NiAl ₂ O ₄	40–60	0.09–0.13	/	[12]
		MgAl ₂ O ₄	37–60	0.09–0.13	NiAl ₂ O ₄	[13]
		TiO ₂	40–60	0.09–0.13	NiTiO ₃	[12]
CuO	0.2	SiO ₂	41	0.083	/	[13]
		Al ₂ O ₃	14–35	0.027–0.08	CuAl ₂ O ₄	[12]
		MgAl ₂ O ₄	43	0.087	CuAl ₂ O ₄	[13]
Fe ₂ O ₃	0.3	SiO ₂	39	0.012	/	[13]
		Al ₂ O ₃	60	0.027	FeAl ₂ O ₄	[14]
		MgAl ₂ O ₄	32	0.0096	FeAl ₂ O ₄	[13]
Mn ₂ O ₃	0.304	SiO ₂	47	0.048	/	[13]
Mn ₂ O ₃		MgAl ₂ O ₄	46	0.047	/	[13]
Mn ₂ O ₃		Al ₂ O ₃	28–60	0.02–0.07	/	[15], [16]
Mn ₂ O ₃		MgZrO ₂	40	0.028	/	[17]

The mentioned oxygen carriers above just included one metal oxide (as oxygen carrier) and one inert substance. Considering the merits and drawbacks of different oxygen carriers, if more than one kind of metal oxide were mixed in different proportion served as the activity component, new oxygen carriers with a better combination property would be prepared. Jin et al. [18] indicated that a new looping material of CoO-NiO/YSZ has an excellent performance including high reactivity, complete avoidance of carbon deposition, and good repeatability. Whereas, Johansson et al. [19] found that the mixed system of 3 wt % nickel oxides with 97 wt % iron oxides produces almost two times as much carbon

dioxide per time unit in comparison to the sum of carbon dioxide when the oxygen carriers were tested separately. Up to now, more than one hundred oxygen carriers have been examined. Many investigations [13], [18], [20] showed that NiO/NiAl₂O₄, Fe₂O₃/Al₂O₃ and CoO-NiO/YSZ performing high reactivity, low attrition rate and a better combination property are ideal metal oxygen carriers. The previous investigations [21], [22] also indicated the different characteristics of various oxygen carrier particles due to different preparation method, sinter temperature, particle size in different reaction using different fuels. However, it gives a great challenge to find the optimal oxygen carrier at a given

CLC system.

The oxygen carrier will be ultimately used in the industrial process, consequently, the production cost of oxygen carrier should be considered. In 2004, Mattisson et al. [23] reported the activity of naturally occurring iron ores such as hematite using multiple reduction and oxidation cycles. The hematite reaction rate to metallic iron is slow and the transformation of hematite to magnetite is a determinate step, where the tendency to agglomerate at high temperature was found. Ni-based oxygen carriers have a preferable reactivity with inconsiderable cost. Recently, Leion et al. [24], [25] used a screening of Fe- and Mn-based ores and industrial products as oxygen carrier, suggesting that all materials had a high reactivity with syngas. Some materials such as the Mn-based Colormax and the Fe-based exhibit a high reactivity with methane made them possible candidates for CLC with gaseous fuel. While other materials, especially the Mn-based ones, revealed poor mechanical stability and poor fluidizing properties. Some Fe-based materials and one of the Mn-based materials, had properties that could make them suitable as oxygen carriers in a CLC system for solid fuels. The ilmenite particles showed no decrease in reactivity in the laboratory experiments after 37 cycles of oxidation and reduction. By frozen granulation, Lyngfelt et al. [26] used commercially available Ni-based raw materials to prepare 36 kinds oxygen carrier particles with properties suitable for the CLC technology. Numerous experiments indicate two of the investigated particles displayed a combination of high reactivity and strength as well as excellent fluidization behavior, which is feasible for a chemical-looping combustion unit. Rydén et al. [27] explored that $\text{La}_x\text{Sr}_{1-x}\text{Fe}_y\text{Co}_{1-y}\text{O}_{3-\delta}$, ceramic materials of perovskite structure having a unit cell with the general formula ABO_3 , provided a high selectivity towards CO/H_2 , which is also suitable for chemical-looping technique. $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$ was demonstrated to be feasible for chemical-looping combustion applications.

Metal oxygen carriers can satisfy the application of the chemical-looping combustion in the industry. However, some metal oxides certainly emitted into atmosphere during the circulating process of metal oxygen carrier. Because the metal oxygen carriers would cause the heavy metal ultrafine particles to emit into ambient environment, attrition and agglomeration hamper the application of metal oxygen carrier to some extent. Accordingly, metal-salt such as sulfate (CaSO_4 , BaSO_4 , and SrSO_4) and phosphate, the new kind oxygen carrier, was introduced to use as oxygen carrier particles. A series of experiments indicated that such kind oxygen carrier with high oxygen carrier capacity and low price relatively can overcome the shortcoming of heavy metal pollution. Zheng et al. [28] made a preliminary investigation into the feasibility of CaSO_4 as the oxygen carrier in thermodynamics and kinetics, and the reducing reaction kinetics through the non-isothermal thermo-gravimetric analysis and infrared Fourier transform. The chemical-looping combustion for the

methane can be realized by the circulating conversion of CaSO_4 and CaS in two interconnection reaction. In such process, the carbon deposition of methane is very severe and the generation of gas sulfide (e.g. H_2S , SO_2) should be prevented. Song et al. [29] summarized the low rate of carbon deposition, formation of gas sulfide and the influence of temperature through the multi-cycle study on chemical-looping combustion for simulated coal gas with a CaSO_4 oxygen carrier in a fluidized bed reactor.

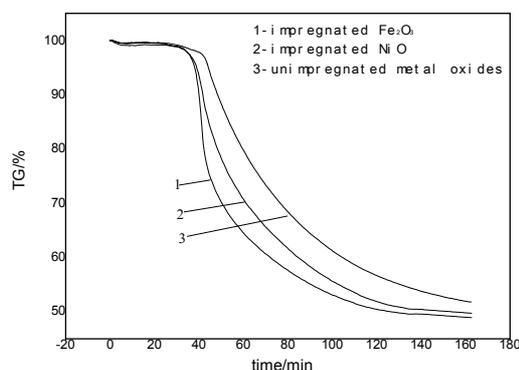


Fig. 2. The TG curves of the reaction of the char and the CaSO_4 oxygen carrier impregnated with and without metal oxides

Considering the advantages of high oxygen transport capacity and low cost of CaSO_4 , it would be promising if the CaSO_4 oxygen carrier can be mixed with some cheap active metal oxides, which may create a synergy effect on enhancing the reactivity and avoiding the side reactions and secondary pollutants. More investigations regarding the decomposition of CaSO_4 and related studies were carried out in our laboratory [30], which gave a deep understanding to the CaSO_4 as a kind oxygen carrier. The mixed oxygen carriers with their different synergy effects were investigated. Fig. 2 indicated that CaSO_4 oxygen carrier impregnated with Ni-based and Fe-based oxides could promote significantly its reduction with char.

IV. The Preparation Method of Oxygen Carrier

The preparation method has an important influence on the properties of oxygen carriers. Previous studies [31] demonstrated that the preparation technique can influence remarkably the performance of oxygen carrier. Fig. 3 [32] showed the differences of $\text{CuO}/\text{Al}_2\text{O}_3$ reductions by three preparation methods. The preparation method determines directly the physical properties such as the particle size, shape, density, mechanical strength and porosity which can influence the reactivity. Until recently, the preparation methods in the literature mainly include: the mechanical mixing method, the impregnation method, dispersion method, frozen granulation method, Sol-Gel method and spray drying process. Generally speaking, the frozen granulation method and the impregnation method were usually used.

The Ni-based and Fe-based oxygen carrier was currently prepared by the frozen granulation method while the Cu-based oxygen carrier by the impregnation method. For preparation process, the mixture ratio, the additive and the calcination temperature were considered as the main influence factors. The referred methods were described as follows.

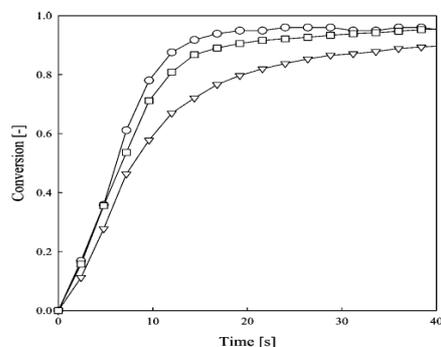


Fig. 3. Reduction reaction of CuO/Al₂O₃ by different preparation methods at 923 K: (○) impregnation method (□) co-precipitation and (▽) solid phase method^[32]

Mechanical mixing method [21], [33] firstly, the metal oxide and inert support in certain particle size (sometimes 10 wt % graphite as additive) is mixed and crushed in the set proportion and added certain water to form pasty mass with proper viscosity. The pasty mass is molded to certain shape and dried softly. Finally, the samples are calcined at high temperature in the muffle furnace. Accordingly, the adequate oxygen carrier is obtained by the sieve method.

Wet Impregnation method [34], [35] the inert support is impregnated with a saturated aqueous solution of metal nitrate, and then is dried and calcined at high temperature in the muffle furnace to make the metal nitrate decomposition, which makes the support generate the active phase. The metal nitrate can be impregnated into inert support for once or many times step-by-step.

Dispersion method [36] the nitrate of metal oxide and inert support are dissolved into solution (e.g. H₂O) and mixed to perform homogeneous distribution. After that, the mixture is dried at different temperature gradient. Finally the oxygen carrier particles were produced by the same process of the mechanical mixing method.

Frozen granulation method [37] the metal oxide, inert support and certain dispersant were mixed with water (sometimes 10 wt % starch as additive) to form the pasty mass using the ball mill. Such pasty is pulverized through the nozzle and frozen to the spherical particle in the liquid nitrogen. Note that the moisture of particles is removed by the freeze-drying and the organic substance is removed by the pyrogenation. Finally, the particles are calcined in the certain temperature, which can gain the desired oxygen carrier.

Sol-Gel method [38] the sol-gel process is a method for the production of inorganic materials at ambient

temperature, which provides a convenient method for incorporation, immobilization, entrapment, and encapsulation of a large variety of materials including organics, inorganics, biomolecules, microorganisms, tissue, and indicators. The sol-gel process, involves the formation of a colloidal suspension (sol) and gelation of the sol to form a wet gel (a globally connected solid matrix), which after drying forms a “dry gel” state (xerogel).

Spray drying process [39] Spray drying process is a method which used the spraying dryer to dry the pasty mass similarly made by the dispersion method. The dried pasty mass is calcined in the certain temperature with the oxygen carrier yield.

Co-precipitation method [33], [40] the nitrate of the desired transition metal in the set weight proportion was made in their solution respectively, and then mixed slowly in one beaker. After the mixed solution was sufficiently stirred, the desired precipitate was obtained through regulating PH value to alter the acidity and alkaline of solution. Then, the resulting solution was maintained with continuous stirring aged for several hours. Subsequently, the precipitate was filtered and washed with distilled water and ethanol.

Among mentioned-above methods, the impregnation method and frozen granulation method was used frequently by many researchers because they operate easily. The particles prepared by the spray drying method show a better performance which is easier to industrialize in the production. Using sol-gel method can get finer and well-distributed particles, however, operate difficultly and cost much.

Different surface topography of oxygen carrier prepared by various methods differs greatly. In general, the shape of oxygen carrier prepared by mechanical mixing method is irregular while prepared other methods has a better degree of sphericity. A preferred porosity and specific surface was realized using the impregnation and frozen granulation method.

The calcination process which fixes the active phase onto the inert support, some researchers also called sinter process, was used in many methods mentioned for preparing the oxygen carrier. In this process the temperature and preparation time will influence the property of the prepared oxygen carrier. It has been demonstrated that the higher temperature and longer calcination time can increase the mechanical strength, however, reduce the reactivity. The proper temperature and lasting time was necessary for preparation. In addition, the additive such as graphite and starch can improve the porosity of the inert or the mixture of oxygen carrier.

V. The Physical Properties of Oxygen Carriers

The physical properties of oxygen carriers mainly included particle size, density, active surface area, pore volume, crushing strength and anti-agglomeration

property which are the important parameters for a successful oxygen carrier. The melting and boiling point of the metal oxide is also an important parameter for oxygen carrier design. Melting point should be high enough to withstand the CLC reaction temperature and avoid agglomeration of circulating particles. Ryu et al. [41] listed the melting point of some metals potentially suitable for using as oxygen carrier. Since the CLC process is operated between 600 and 1200 °C, consequently, the melting point of the metal selected is close to or lower than the operation temperature. For example, Cd, Zn and Ce with melting points below than or equal to 600°C, are unsuitable as CLC materials. Also, Cu has a relatively low melting point (1085°C), the operation temperature should be considered in case agglomeration.

The particle size and density determine the fluidizability of the oxygen carrier which influences the overall reaction rate, given their influence on mass and heat transfer inside the particles.

Varma et al. [42] used the Friedman isoconversional method to demonstrate the presence of internal and external mass-transfer limitations during the reaction, whose findings also emphasized the importance of assessing diffusional effects in the determination of reaction kinetics.

Summarizing the literatures, oxygen carriers with particle size ranging from 0.08 to 2mm and density ranging 1.5 to 4.5 kg/dm³ are suitable for CLC. For commerce using, the high density is not available for the fluidized bed combustion.

Fig. 4 [43] depicted the effect of particle size on gas conversion as a function of time, which used CaSO₄ as the oxygen carrier for the CH₄ combustion, suggesting that the decrease of the particle size resulted in the increase of the conversion of CH₄.

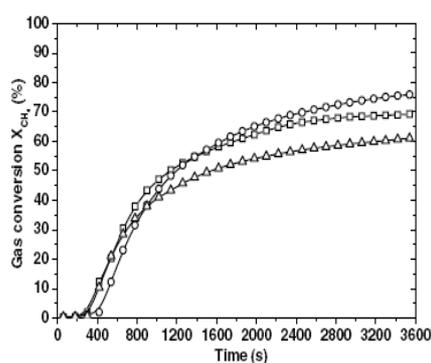


Fig. 4. The effect of sample particle size on the conversion of CH₄ to CO₂ as a function of time. (□) 0.2-0.4 mm (○) 0.4-0.6 mm (▽) 0.6-0.8 mm [43]

The physical stresses associated with fluidization require the oxygen carrier particles with the higher crushing strength, usually ranged from 3.7-5.2N. A high crushing strength determined a better continuous

circulating capability of the oxygen carrier in the dual interconnected fluidized bed.

However, the abrasion of the particles is unavoidable in the reaction process with the fuel.

Partial abrasion occurred in the dual interconnected fluidized bed more or less after multiple redox cycles of particles. Friction between particles and vessel wall and inter-particles friction is account for the abrasion.

Mattisson et al. [19] collected the crushing strength of many oxygen carriers. It is concluded that Cu-based and Mn-based oxygen carriers have a bad stress characteristics at the higher temperature while Fe-based and Ni-based oxygen carriers show a better physical stress characteristics.

Anti-agglomeration is an important property for the oxygen carrier.

If the agglomeration appeared in the reactor, the property of oxygen carrier and fluidization behaviors will change significantly.

Fig. 5 described light microscope image of micro-agglomerate.

It was presented that the physical property of the particles was ruined severely.

The exact mechanisms of particle agglomeration are not yet well understood. Linderholm [44] examined that the degree of oxidation has an influence on agglomeration and more reduced particles seem to form agglomerates easier.

Other factors that may influence agglomeration behaviors are particle size and shape, and fuel reactor mixing conditions.

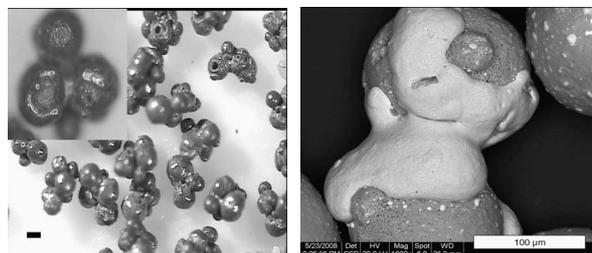


Fig. 5. Light microscope image of micro-agglomerates encountered in the air reactor upon opening after 1016 h of operation. The black line in the lower left corner represents 100 μm. The magnification of the inset (top left) is approximately twice that of the main picture [39]

The defluidization of the particle in the dual interconnected fluidized bed is undesirable. However, the defluidization was associated with agglomeration of the bed. Cu-based oxygen carrier has low melting point that is prone to agglomerate at high temperature, causing defluidization. Mattisson et al. [45] investigated the defluidization condition for a fluidized bed of Fe-based, Ni-based, and Mg-based oxygen carriers. There was no defluidization of the Fe-based particle when hematite was reduced primarily to magnetite and any further formation of wustite was limited. The defluidization of the Fe-based particle occurred during the oxidation period after multiple reduction cycles, in which significant further reduction of the magnetite to wustite

occurred. The defluidization of particle is also dependent on the carbon formation. The amount of oxygen carriers needed in each reactor and the solid circulation rate between the two reactors mainly depend on the actual oxygen carrying capacity of carriers. In CLC process, the oxygen capability is usually defined as follows:

$$R_0 = \frac{m_{ox} - m_{red}}{m_{ox}} \quad (5)$$

Where m_{ox} and m_{red} is the mass of oxidized and reduced oxygen carriers, respectively. Different oxygen carriers may be reduced to different states. For example, only hematite convention to magnetite is meaningful as the Fe-based oxygen carrier. Actually, only partial oxygen in the Fe-based oxygen carrier can be used during the redox process. The oxygen carrying capacity of typical oxygen carriers were listed in Table II. Among the given oxygen carriers, CaSO_4 has a higher oxygen carrying capacity.

VI. The Reaction Fuel

The fuel has an important influence on the chemical looping combustion using various oxygen carriers. In the beginning, the gas (e.g. CH_4 or H_2) was usually used as the fuel to investigate the characteristics of the metal oxygen carrier. With the research advances, the synthetic natural gas or synthetic water gas was widely employed in the study of CLC system. Nevertheless, the research into the solid fuel such as coal and biomass was scarce due to several technical problems. There are three approaches to chemical looping combustion for solid coal. The first approach is to gasify coal in a separate gasifier with pure oxygen to produce a synthetic gas, i.e. CO , H_2 and CH_4 , without nitrogen. The synthetic gas is supplied for the CLC system, as in the CLC process using a natural gas. However, the production of pure oxygen and the fabrication of an additional gasifier will require, thus dramatically increased the cost of the CLC system. The second approach is to directly utilize coal in the fuel reactor in the CLC system. It has economic advantages, but has several technical problems. There are two reaction paths in fuel reactor, direct reduction of oxygen carrier by coal concerning technically the low reactivity between coal and oxygen carrier due to the low efficiency of solid-solid contact and indirect reduction by the synthetic gas of coal gasification in the fuel reactor concerning technically that the coal gasification rate is lower than its combustion rate at the same temperature. Such issues might prolong the residence time of coal inside the fuel reactor to fulfill the higher carbon conversion efficiency. The third approach is the chemical-looping with oxygen uncoupling (CLOU) proposed by Mattisson [46] that an oxygen carrier such as $\text{CuO}/\text{Cu}_2\text{O}$ can decomposes to a reduced metal oxide and gas-phase oxygen in the fuel reactor, thus gas-phase oxygen can react with the solid fuel. There exists many

technical problems, the chemical-looping combustion for solid fuel still has a promising development potential. The U.S. Department of Energy and National Science Foundation of USA have granted the chemical-looping combustion for solid fuel, among which Fan's Group of Ohio State University proved the feasibility of hydrogen production by the chemical-looping combustion for the solid fuel. The Combustion and Environment Collage of Western Kentucky University has proposed the initiative approach to the chemical-looping combustion for the coal fuel [47]-[49]. Shen et al. [50] simulated the processes for chemical looping combustion of coal, including coal gasification and reduction of oxygen carrier with Aspen Plus software. The effects of air reactor temperature, fuel reactor temperature, and ratio of water to coal on the composition of fuel gas, recirculation of oxygen carrier particles were discussed. Leion et al. [31] investigated the feasibility of using petroleum coke via the gasification intermediates, CO and H_2 , as fuel in chemical-looping combustion, and found that the presence of a metal oxide enhanced the gasification of petroleum. Furthermore, Pan et al [51] investigated Chemical Looping Combustion used coal, biomass, and solid Waste as solid fuels and indicated the feasibility of many solid fuels for CLC and concluded that the solid fuels with higher reactivity (higher volatile matter) would be desirable for the development of the chemical looping combustion process of solid fuels.

VII. Chemical Reaction Thermodynamics

The reaction characteristic of oxygen carrier should be investigated under different gas atmospheres and operation conditions using analyzed the thermodynamic and kinetics. Chemical reaction thermodynamics is important on the understanding of the reaction mechanism, the product composition as well as the design of technical parameters in chemical-looping combustion fuel. With the standard Gibbs free energy changes, the equilibrium constants can be calculated for various reactions of metal oxide reduction and coal gasification over a wide range of operating temperatures. The relationship between the equilibrium constant K_p and temperature T is expressed as:

$$R \ln K_p = -\frac{\Delta H_T^\circ}{T} + \Delta S_T^\circ \quad (6)$$

Where ΔH_T and ΔS_T are the standard formation heat, the standard formation entropy at the corresponding reaction temperature, respectively, and R is the gas constant. With respected to thermodynamic parameters, the standard formation heat ΔH_T and the equilibrium constant K_p can be calculated. Fig. 6 shows the equilibrium constants ($K_p = \exp(-\Delta G/RT)$) as a function of temperature for the reduction of metal oxides with CO .

As illustrated in Fig. 6, the equilibrium constants of

metal oxide reduction with CO have a monotonously decreasing trend with increasing temperature, which is in accordance with the exothermic process of the reductions of metal oxide with CO. Compared with the metal oxide reductions, the equilibrium constants of major reactions of coal gasification in the fuel reactor under ambient pressure are also presented in Fig. 6. The metal oxides based on Ni, Fe, Co, Cu and Mn has a good affinity with CO, and is thermodynamically feasible as oxygen carrier. However, Mn₂O₃, Co₃O₄ and CuO will decompose at temperatures above 820, 890 and 1030°C, respectively. These oxides are unsuitable as oxygen carriers in the process of chemical looping combustion of coal at high temperature.

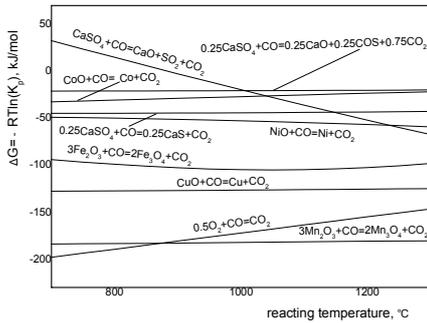
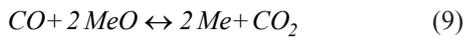
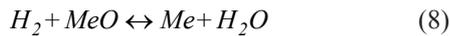


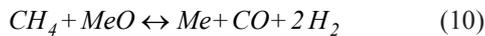
Fig. 6. Variation of equilibrium constant K_p for reduction of metal oxide by CO as a function of temperature

Gayán et al. [9] analyzed the main reactions in the dual interconnected fluidized bed during the oxygen carrier reduction period. The referred reactions are as follows:

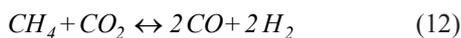
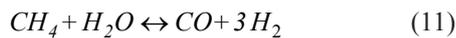
Oxidation reaction:



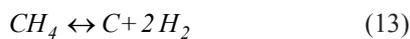
Partial oxidation reaction:



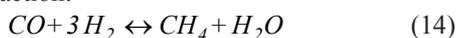
Catalytic reforming reaction:



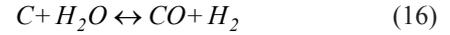
Catalytic decomposition reaction:



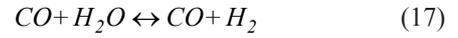
Methanation reaction:



Carbon gasification:



Water gas shift reaction:



Carbon formation:



All the main reactions using gas from coal gasification as fuel were summarized above. The reactions (7), (8), (9) are the mainly reactions in chemical looping combustion. However, other reactions will happen with changing atmosphere in the reactor. The main reaction is carried out at reduced atmosphere, whose reactivity of oxygen carriers should be investigated under different gas atmospheres. In the last nine reactions (Eqs. (11)-(18)) the metal acts a catalyst rather a reactant. These reactions are considered undesirable and can be suppressed by adjusting reaction parameters such as temperature, pressure, gas flow in the reactor and the design criteria for the CLC system. The reactions (13) and (17) are mainly responsible for the carbon formation. The reaction (19) is the main reaction in the air reactor. The reduction of oxygen carriers is illustrated by Oxygen potential ($\Delta G^\theta = RT \ln P_{O_2}$), where R and T are the gas constant and the corresponding reaction temperature, respectively; and P_{O_2} the equilibrium partial pressure of O_2 :

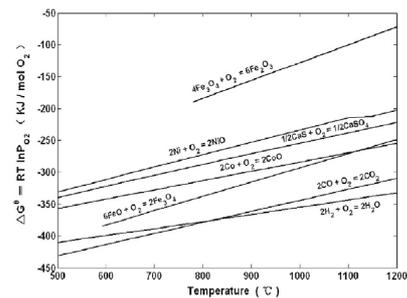


Fig. 7. Oxygen potential of the metal-based and calcium-based oxygen carriers as the function of temperature [52]

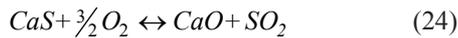
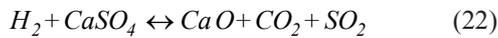
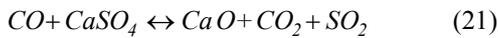
As illustrated in Fig. 7, the lower the oxygen potential of the oxygen carriers at a certain temperature, the more difficult the reduction of the oxygen carrier. The Fe, Ni, CaS and Co based oxygen carriers have good affinity with the reductive agents CO and H_2 which are thermodynamically feasible as oxygen carriers.

In addition to above reactions, the interaction of

metal-support and the effect of fuel gas composition are also taken into account. José M. Palacios [53] revealed the interaction of metal-support as follows:



García-Labiano [54], [55] studied the fate of sulfur in the CLC system and indicated that Nickel sulfide, Ni₃S₂, was formed at all operating conditions in the fuel reactor, which produced an oxygen carrier deactivation and lower combustion efficiencies. However, the oxygen carrier recovered their initial reactivity after certain time without sulfur addition. The sulfides were transported to the air reactor where SO₂ was produced as final gas product. A summary of the fate of light hydrocarbons was as follows:



CaS is the required reductions of CaSO₄ with CO and H₂ yield in the fuel reactor. It should be pointed out that the parallel reaction (21) and (22) will occur. In the air reactor, the side reactions (23) and (24) will also occur to produce SO₂. Shen et al. [52] indicated that SO₂ can be reproduced to CaSO₄ by adding a small amount of fresh limestone into the system of CLC. Moreover, the reaction atmosphere should be account for quickening side reaction rate. The potential reactions and influence factors can be obtained from the thermodynamic analysis, which can give a guide on the investigation of the chemical-looping combustion.

VIII. Reduction and Oxidation Kinetics

The reactions of oxygen carrier reduction in the fuel reactor are governed by the prevailing chemical thermodynamics and by the reaction kinetics, where the reactions of oxygen carrier reduction in the fuel reactor were just about gas-solid phrase. The reaction rate (dX/dt) is defined as:

$$\frac{dX}{dt} = -\frac{1}{m} \frac{dm}{dt} \quad (25)$$

Where $X = \frac{m - m_{red}}{m_{ox} - m_{red}}$ represented the degree of conversion. For modeling the present gas-solid reaction kinetics, three different gas-solid reaction models [56], [57]:

The shrinking core, uniform reaction, and modified

volumetric models, was used in the definite reaction of the oxygen carriers with certain fuel. The reaction kinetics of the three models was introduced as follows:

1. The reaction kinetics for the shrinking core model was represented by:

$$\frac{dX}{dt} = k_r (1-X)^{2/3} \quad (26)$$

Where the reaction constant k_r can be derived as:

$$k_r = \frac{3}{t} [1 - (1-X)^{1/3}] \quad (27)$$

This model incorporates the dependence of particle size and pore structure of the solid reactant particles on the rate of reaction. Based on this model, as the reaction progresses the metal-metal oxide interface moved towards the center of the grain, leaving behind a porous metallic/metal oxide product layer through which gaseous reactants and products diffused.

2. Reaction kinetics for the uniform reaction model and its reaction constant were as follows:

$$\frac{dX}{dt} = k_v (1-X) \quad (28)$$

$$k_v = -\frac{1}{t} \ln(1-X) \quad (29)$$

For the modified volumetric model, the experimental data (X - t) can be expressed as the following equation, and the values of the constants a and b are determined by the least-squares method:

$$X = 1 - \exp(-at^b) \quad (30)$$

3. The reaction rate for the modified volumetric model was derived as:

$$\frac{dX}{dt} = a^{1/b} [-\ln(1-x)]^{(b-1)/b} (1-X) \quad (31)$$

Kim et al. [57] studied the kinetics of NiO-Fe₂O₃/bentonite reacting with the CH₄ and concluded that the modified volumetric model is the best representation of the reduction of these particles while the shrinking core model is a better representation for the oxidation of these particles. Garcia-Labiano et al [58] studied the CLC kinetics taking into consideration the structural variations of the oxygen carrier. Plate and spherical geometries were studied by the changing grain size model. These shapes were dependent on the oxygen carrier preparation method and subsequent characterization results. More recently, Hossain and De Lasa [59] and Sedor et al [11], [12] developed phenomenological kinetic models applied in a CLC process. The nucleation and nuclei growth model and unreacted shrinking core models were developed based on the physicochemical characteristics

of the prepared oxygen carriers and the observed reaction rates under various experimental conditions.

IX. The Further Application of CLC

Due to high efficiency, inherent CO_2 separation and low NO_x emission, chemical-looping combustion (CLC) technique can be combined with the present power generation system, such as combustion turbine (CT) and solid oxide fuel cell (SOFC). Other chemical looping based techniques, chemical-looping reforming and lime-based CO_2 looping cycles were exploited. By the analysis for these systems mostly based on hypothesis using the simulation software, it gives a guide on the research and development for the CLC technique. Three chemical looping gasification processes, i.e. Syngas Chemical Looping (SCL) process, Coal Direct Chemical Looping (CDCL) process, and Calcium Looping process (CLP), are being developed at the Ohio State University [60]. These processes utilized simple reaction schemes to convert carbonaceous fuels into products such as hydrogen, electricity, and synthetic fuels through the transformation of a highly reactive, highly recyclable chemical intermediate. A hydrogen production process by steam reforming of natural gas with inherent capture of carbon dioxide by chemical-looping combustion was proposed in several literatures [61]-[63]. This process is considered as a promising for hydrogen production. The schematic diagram of chemical-looping hydrogen production was showed in Fig. 8. Using chemical-looping concept to produce hydrogen is mainly divided into two paths: one is producing hydrogen from fuel gas directly and the other from the stream reacting with the reduced oxygen carriers, mainly using Fe-based.

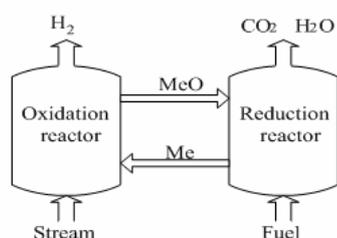


Fig. 8. Schematic diagram of chemical-looping for hydrogen production

Paolo Chiesa [64] proposed a three-reactors CL system, where iron oxide particles were circulated to: (i) oxidize natural gas (thus providing, after cooling and water condensation, a CO_2 stream ready for sequestration), (ii) reduce steam, to produce hydrogen as the final product of the process, (iii) consume oxygen from an air stream, to sustain the thermal balance of the system. Cleeton et al. [65] simulated chemical looping combustion (CLC) system, using haematite (Fe_2O_3) as an oxygen carrier in conjunction with a steam-coal gasification process. At present, the concept of chemical-looping for hydrogen production is still at the

initial stage. Further advance should be carried out from the present simulation stage.

X. The Conclusion and Outlook

Chemical-looping combustion (CLC) featuring inherent CO_2 separation is considered as one promising of the CO_2 sequestration technologies. The preparation of a suitable oxygen carrier for CLC is a key issue to realize the CLC in the industry and still a major focus of current research. The following conclusions were presented.

- I. Among the researched materials for oxygen carrier, the Ni-based, Fe-based and Cu-based oxides is the main materials used as the oxygen carrier. Other materials such as ceramic materials were investigated. The selection of the material of oxygen carriers will focus on the ore and industry products with low cost. While, the Fe-based and CaSO_4 materials with lower cost and acceptable reactivity are the promising materials for CLC.
- II. The preparation methods of the oxygen carrier included almost the ones for preparing materials. Given used in the industry in the future, the impregnation method and Spray drying method was widely used by many researchers. The oxygen carriers using the different methods and materials performance the different property, hence advance research on the synthesis methods of preferable oxygen carrier needs to be carried out. The preparation of nano-composite oxygen carriers is a novel aspect.
- III. The performance of the same oxygen carrier will be different with different fuel used in the CLC. The chemical-looping combustion for solid fuel such as coal and petroleum coke facing technical challenge, however, the trend in the future, is being investigated. Particle size, density, active surface area, pore volume, crushing strength and anti-agglomeration should be fit for the redox reaction in the dual connected fluidized bed. The reaction characteristics of oxygen carrier were analyzed from the thermodynamics and kinetics. Furthermore, the reaction kinetics between the fuel, especially solid fuel, and the oxygen carriers need further investigation.
- IV. Based on the concept of the chemical looping technique, hydrogen production with inherent CO_2 separation was considered as a novel one. The feasibility of it has been verified by some researchers. This hydrogen production technique will obtain the further advance in the future.

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