Development of Ni-based redox catalysts for chemical looping processes

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**DEVELOPMENT OF NI-BASED REDOX CATALYSTS
FOR CHEMICAL LOOPING PROCESSES**

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SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING

2019

Development of Ni-Based Redox Catalysts for Chemical Looping Processes

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A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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Authorship Attribution Statement

This thesis contains material from 3 papers published in the following peer-reviewed journals where I was the first author.

Chapter 4 is published as J. Huang, W. Liu, Y. Yang, Phase interactions in Mg-Ni-Al-O oxygen carriers for chemical looping applications, Chem. Eng. J. 326 (2017) 470-476.

The contributions of the co-authors are as follows:

- Prof. Yang Yanhui provided the project direction and edited the manuscript drafts.
- I conducted the material synthesis and performance test. Dr. Liu Wen collected the XRD data and performed the phase analysis.
- I prepared the manuscript drafts. The manuscript was revised by Dr. Liu Wen.

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The contributions of the co-authors are as follows:

- Prof. Yang Yanhui pointed the research area and supervised this work.
- I prepared the oxygen carrier, collected the SEM images, and conducted the TGA and chemical looping tests.
- SXRD data was collected by Dr. W. Hu and Dr. I. Metcalfe from Newcastle University. They also reviewed the manuscript before submission.
- SXRD data analysis was completed by Dr. Liu Wen, obtaining the lattice parameters of the phases in the oxygen carriers.
- I wrote the drafts of the manuscript. The manuscript was revised together with Prof. Liu Bin and Dr. Liu Wen.

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- Prof. Yang Yanhui pointed the research area and supervised this work.
- I conducted the material synthesis and characterization. Dr. Liu Wen helped with the data analysis and results discussion.
- I wrote the drafts of the manuscript. The manuscript was revised by Prof. Liu Bin.

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Abstract

Chemical looping concept describes a class of processes that uncouples an overall homogeneous reaction into heterogeneous sub-reactions, using a solid intermediate, namely oxygen carrier or redox catalyst shuttling between the sub-reactions to transfer the reaction species. Take chemical looping combustion (CLC) as an example, the fuel and air will react with the oxidized and reduced oxygen carrier in separated gas stages or reactors, generating a concentrated CO₂ stream after H₂O removal by condensation during the fuel combustion. The thermodynamic fuel conversion efficiency increases but the NO_x formation is hindered due to the relative low working temperatures compared with the traditional single-stage combustion. Thus, CLC offers the benefits of fuel combustion with inherent CO₂ capture and significantly reduced NO_x formation over conventional combustion.

The formulation and phase interactions in the oxygen carriers play important roles in determining the activity of the lattice oxygen, so as the performance of the oxygen carriers. In Chapter 4, NiO-MgO-Al₂O₃ oxygen carriers were synthesized using layered double hydroxides (LDH) as precursors to facilitate the formation of molecular level dispersion of cations in the resulting oxygen carriers after calcination. The performance of the synthesized oxygen carriers was investigated over 100 chemical looping cycles of 5 vol.% H₂/N₂ reduction and 5 vol.% O₂/N₂ oxidation. The morphology and phase composition of the fresh and spent oxygen carriers were characterized by SEM, XRD and TPR. Rietveld refinement of the XRD patterns and

TPR confirmed the presence of halite (MgO-NiO) and spinel (MgAl_2O_4 - NiAl_2O_4) solid solutions, the composition of which changed over cycles and determined the cycle behavior of the oxygen carriers.

Using CH_4 as the fuel, NiO performs poorly in CLC due to the severe carbon deposition from CH_4 decomposition catalyzed by the reduced Ni particles. The performance may be modified by CuO which provides selective lattice oxygen for CLC. Chapter 5 reports a systematic investigation of NiO-CuO- Al_2O_3 mixed oxide oxygen carriers over chemical looping oxidation of CH_4 . The oxygen carriers were prepared from Ni/Cu/Al LDH precursors, which were synthesized via the hydrothermal reactions using urea as the precipitant. The solids' compositions were analyzed by a set of complementary experimental techniques (SXRD, TGA, TPR). It was found that the formation of NiAl_2O_4 is favored over that of CuAl_2O_4 after calcinations at 1000 °C. The results also suggest that the mixing of NiO and CuO leads to enhanced lattice oxygen activity in both oxides. However, the lattice oxygen activity in the $(\text{Ni,Cu})\text{Al}_2\text{O}_4$ spinel was reduced due to the formation of solid solution $\text{Ni}_{1-x}\text{Cu}_x\text{Al}_2\text{O}_4$, which appears to be an excellent retardant for carbon deposition. The findings in this study are useful to the design of high performance oxygen carrier that exploits the phase interactions in the Ni-Cu- Al_2O_3 system.

In traditional steam reforming of methane (SRM), with CH_4 and steam co-fed into the reactor, the selectivity to CO and H_2 are thermodynamically limited in the presence of water gas shift reaction. In Chapter 6, a series of Ni-Fe redox catalysts with varying Ni/Fe ratios were designed and prepared by co-precipitation, which

could selectively convert CH_4 to syngas via chemical looping steam reforming coupled with catalytic CH_4 decomposition. Carbon deposit in the CH_4 reduction stage was selectively gasified to syngas in the following oxidation with hot steam, so that the overall selectivity to CO was dramatically enhanced in the chemical looping scheme. The optimized redox catalyst with equimolar Ni and Fe could achieve high CH_4 conversion up to 97.5% and CO selectivity up to 92.9% with excellent stability at 900 °C, with productivity of 9.6 and 29.0 mol $\text{kg}_{\text{catalyst}}^{-1}$ per cycle for CO and H_2 , respectively.

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Chapter 1 Background and Philosophy

1.1 Background on chemical looping

The rapid development of human civilization brought about many adverse effects on our planet. Today, the energy consumption of our society is still heavily relying on unrenewable fossil fuels, such as crude oil, coal, natural gas and shale gas. The excessive combustion of fossil fuels since the industrial revolution has discharged huge amount of greenhouse gases into the atmosphere, predominantly CO₂ [1]. Catastrophic consequences of the greenhouse effects include the diminishing arctic ice shield, sea level rise, global temperature rise, as well as increased occurrence of extreme weather events [2]. For the global sustainable development, there is an urgent need for us to implement means to reduce the CO₂ emission, to improve the efficiency of current fossil fuel energy conversion and to develop renewable energy resources. However, any reasonable projection of renewable energy does not suggest that fossil fuels can be phased out in the coming decades. To combat the climate change, carbon capture and storage (CCS) technology is still of significant interest and has been proposed as a mid-term strategy to solve the energy and environmental issue of greenhouse effect [3, 4].

There are three technologies for carbon capture during the conversion of fuels, *i.e.* pre-combustion, post-combustion and oxygen combustion [3-8]. In pre-combustion carbon capture, the chemical energy of fossil fuels is converted into

H₂, which is used for clean combustion. While in post-combustion carbon capture, the CO₂ in the combustion flue gas is scrubbed by porous or basic materials via adsorption or absorption. In oxygen combustion technology, pure oxygen instead of air is fed to the combustion system, resulting a highly CO₂ concentrated flue gas. However, the separation of O₂ from the air is achieved by cryogenic gas separation, which is associated with large energy penalty and will reduce the efficiency of the whole combustion system. Therefore, these technologies have the disadvantage of high operation cost due to the energy-intensive gas separation processes.

Chemical looping combustion (CLC) has widely attracted research attention as an innovative fuel conversion technology with inherent CO₂ separation, meaning negligible energy penalty compared to the traditional gas separation processes [9-15]. Due to the reduced reaction temperature, NO_x formation can also be significantly reduced. In a typical CLC process, the combustion reaction of fuel with air takes place in two sub-reactors with a solid intermediate circulated between them. Generally, the oxides of first-row transition metals, *viz.* Mn, Fe, Co, Ni and Cu are used as the solid intermediates in CLC [13, 16, 17]. Firstly, the fuel reacts with the metal oxides to generate CO₂, water vapor as well as the heat for power generation, and simultaneously the metal oxides are reduced to lower valence states. After removing the water vapor by condensation, high-purity CO₂ stream can be obtained and ready for sequestration. To close the loop, the reduced metal oxides will then react with air to recover their original state. Therefore, in CLC, the fuel will never be in contact with air, and CO₂ stream will never be diluted by N₂. Thus, the expensive cost of gas

separation is inherently avoided.

The solid intermediate, also called oxygen carrier or redox catalyst, is vital to the successful implementation of chemical looping processes. The sought-after criteria for choosing oxygen carrier material have been established: high redox reactivity, high oxygen transfer capacity, sufficient cyclic stability, low cost and thermal/mechanical stability and robustness [9-11, 13, 14]. Due to the harsh reaction conditions, it is difficult to fulfill all the criteria. Pure metal oxide can hardly afford satisfactory performance against sintering and defluidization. The active metal oxides are usually supported on common catalyst supports, such as Al_2O_3 , SiO_2 , ZrO_2 , TiO_2 , CeO_2 and MgAl_2O_4 . In order to lower the cost of the oxygen carrier, mineral ores were also investigated both in laboratory and pilot scale [18-20]. However, the optimization of the reactivity and cycle stability of ores is limited due to the complexity of the material composition, low fraction of the active metal oxides and low surface area. Therefore, it is still desirable to develop suitable synthetic oxygen carrier materials which can provide excellent reactivity and cyclic stability at reasonable cost.

1.2 Aims and outlines

The properties of the oxygen carrier, including the oxygen transfer capacity, activity of the lattice oxygen in the reduction, activity of the reduced oxygen carrier being regenerated in the oxidation, stability, are critical parameters for the performance of chemical looping processes, i.e. the fuel conversion and product selectivity under the evaluated reaction conditions. Both the composition and phase

interaction have fundamental effects on the property of the oxygen carrier. To develop high-performance oxygen carrier, it is a prerequisite to have a better understanding of the phase interaction of the components in the oxygen carrier over chemical looping cycles.

In Chapter 4, NiO-MgO-Al₂O₃ oxygen carriers were studied over redox cycles with 5 vol.% H₂/N₂ and 5 vol.% O₂/N₂. H₂ other than CH₄ was used as the fuel for simplicity, avoiding any carbon contamination on the oxygen carrier. The NiO/Al₂O₃ oxygen carrier (Ni₃Al) showed constant solid conversion in 100 cycles, while MgO-modified oxygen carriers (Ni₂MgAl and Ni_{2.5}Mg_{0.5}Al) presented an activation period in the initial 10 redox cycles. The fresh and spent samples were characterized by Rietveld refinement of the XRD patterns and TPR. It was found that the NiO-MgO-Al₂O₃ oxygen carriers include a halite (NiO-MgO) and a spinel (NiAl₂O₄-MgAl₂O₄) solid solutions. Both XRD and TPR analysis suggested a net migration of Ni²⁺ from the spinel to the halite after the redox cycles, which was correlated with the change of the performance in the chemical looping test. This work implicates that MgAl₂O₄ could not be considered as the inert support for NiO, and MgO modification benefits the sintering resistance of the oxygen carrier.

Binary oxygen carriers offer tunable redox activity of the lattice oxygen, compared with the single oxide oxygen carriers which can only supply lattice oxygen at specific oxygen partial pressure. In Chapter 5, a series of NiO-CuO-Al₂O₃ mixed oxides were investigated in chemical looping oxidation of CH₄. SXRD analysis revealed the mutual doping between CuO and NiO, which promoted the activity of

lattice oxygen in both phases as observed in TPR with 5 vol.% H_2/N_2 . Furthermore, the formation of $\text{Ni}_{1-x}\text{Cu}_x\text{Al}_2\text{O}_4$ spinel solid solution resulted in lower activity of lattice oxygen, which could boost methane reforming and contribute to the suppression of carbon deposition. The findings in this chapter are useful to the design of high performance oxygen carriers that exploit the phase interactions in the $\text{NiO-CuO-Al}_2\text{O}_3$ system.

Carbon deposition is usually an undesirable side reaction in CLC because the remove of carbon by air will not only hinder the overall carbon capture efficiency, but also accelerate the sintering of the oxygen carrier. In Chapter 6, the carbon deposit during 5 vol.% CH_4/N_2 reduction on a series of Ni-Fe redox catalysts was purposely utilized to produce syngas in the subsequent gasification with steam. CH_4 conversion of 97.5% and CO selectivity of 92.9% were achieved with the optimized equimolar Ni-Fe catalyst at 900 °C with excellent cycling stability. The effects of composition (Ni/Fe ratio), reaction temperature (700-900 °C), catalyst regeneration with O_2 were systematically investigated. In the chemical looping scheme, the water gas shift reaction can be minimized so that favouring high CO selectivity. The performance was superior to the conventional co-feeding steam reforming of CH_4 , in which the selectivity is highly limited by thermodynamics.

Chapter 2 Literature Review

CO₂ separation can be eliminated from fuel conversion via CLC, due to the fact that the overall combustion reaction is broken down to sub-reactions conducted in isolated steps or space, minimizing the energy penalty for carbon capture. Chemical looping has attracted a lot of research attention as it offers a versatile platform for fuel conversion and carbon capture in the last two decades. In a chemical looping scheme, one can realize not only various processes by pairing different reduction and oxidation steps for special aims, such as carbon-captured combustion, fuel reforming, water/CO₂ splitting and air separation, but also the control of the product distribution by developing functional oxygen carriers with tuned oxygen reactivity both in the bulk and on the surface. In this chapter, thermodynamic perspective of CLC will be introduced, followed by the review of various chemical looping processes. The development of oxygen carriers will then be elaborated with different component categories.

2.1 Chemical looping processes

2.1.1 Thermodynamic perspective of CLC

In CLC, the oxygen needed for the fuel combustion is transferred by the oxygen carriers in two steps, i.e. a reduction and a regeneration step happened in the fuel reactor and air reactor, respectively, as shown in Figure 2.1. High purity CO₂ can be obtained from the flue gas of the fuel reactor after water removal for inherent carbon

capture, while the heated lean air from the air reactor will be sent to the gas turbine for power generation. The oxygen carrier reacts with the fuel and the air according to the following reaction equations:

Figure 2.1 Illustration of chemical looping combustion system for carbon capture.

In the fuel reactor, the fuel is oxidized by the oxygen carrier. This reaction can be endothermic or exothermic depending on the fuel type and the oxygen carrier, while the regeneration reaction of the oxygen carrier in the air reactor is always exothermic. The overall heat of the two sub-reactions is identical to that of the conventional combustion reaction. However, the equilibrium temperature of the sub-reaction is much lower than the reaction that the fuel burns with air directly. Taking CH_4 combustion as an example, the equilibrium temperature can be calculated as high as 160,000 K. As the reaction temperature is limited by the turbine inlet temperature, the temperature of conventional combustion is usually far below that required for reversibility, thereby causing significant entropy generation and Gibbs free energy loss [21].

In 1983, Richter and Knoche [22] pointed out that the irreversible entropy production of combustion can be decreased if the contact of fuel with oxygen is prevented and intermediate chemical reactions are supported. From this point of view, the combustion efficiency can be increased through CLC to produce more mechanical work output.

2.1.2 Typical chemical looping processes

The development of chemical looping concept could date back to the early 20th century. It was firstly proposed by Howard Lane for the purpose of H₂ production through steam-iron reaction [23]. This technology was used until 1920s when H₂ production from oil and natural gas became more economically competitive. In 1950s, chemical looping strategy was applied to produce pure CO₂ for the beverage industry in a patent by Lewis and Gilliland [24], applying iron and copper oxides as the oxygen carriers. In 1987, the technical term "chemical looping" was introduced by Ishida and Jin [25, 26], who proposed CLC for the CO₂ capture application. In order to overcome the shortage of the slow kinetics in the solid-solid reaction for solid fuels, Lyngfelt and co-workers [27] proposed chemical looping with oxygen uncoupling concept in 2005. Cu-, Mn- and Co-based oxygen carriers were used in this application because these oxides can be thermolyzed at high temperature, typically over 900 °C, generating molecular O₂. The oxygen partial pressure is relative high, so that the reaction rate can be obviously improved when coal is utilized as the fuel. In 2006, chemical looping steam reforming was invented by Ryden [28], in which H₂ was

produced with CO₂ capture by CLC. Fan and co-workers [29] reported CLC of syngas for the production of high purity hydrogen, with a continuous cycle of syngas reduction, steam oxidation and air regeneration in a fixed-bed reactor. Moghtaderi [30] reported chemical looping air separation in 2010, concluding that Mn, Co systems and their mixtures are suitable for air separation application.

Figure 2.2 Typical chemical looping processes with oxygen carriers MO_x and MO_y ($y > x$) involved. (a) Full combustion, in which high-purity CO₂ can be captured after H₂O removal by condensation, (b) fuel partial oxidation for syngas production, (c) CO₂/H₂O reforming, in which fuel partial oxidation is coupled with CO₂/H₂O splitting to generate CO/H₂, (d) air separation by taking advantage of oxygen uncoupling of metal oxides at high temperature, (e) selective oxidation of hydrocarbons and (f) sorption-enhanced steam reforming.

In CLC, the separation of CO₂ from the gaseous mixture of CO₂, water vapor and N₂ can be avoided via oxygen carrier mediated stepwise sub-reactions. Theoretically, any carbonaceous fuels which can be oxidized by the lattice oxygen of transition metal oxide can be used as the feedstock. Up to date, various kinds of fuels in gas, liquid and solid phase have been applied as the feedstock, such as natural gas, syngas, ethanol, coal, char, biomass and solid wastes. However, the most researched feedstock is gaseous fuel, as the reaction rate of the solid-solid reaction is limited due to the slow oxygen transfer from the oxygen carrier to the solid fuels. For the solid fuels, Mn-, Cu- and Co-based oxygen carriers are promising due to their ability to decompose at high temperature and release gaseous oxygen, accelerating the reaction between the fuel and oxygen carrier. In CLC, air is the oxidant to regenerate the oxygen carrier. Instead of air, H₂O and CO₂ can also be used as soft oxidants in chemical looping systems with the purpose of H₂ production and fuel reforming [31, 32]. Air separation can be achieved with the heat from solar energy or fuel combustion [33]. Coupling chemical looping and catalysis, selective oxidation of hydrocarbon by the oxygen carrier can afford value-added chemicals, such as higher alkanes, alkenes, epoxides and other oxygenated products [15]. Typical examples for chemical looping selective oxidation are CH₄ coupling or dehydroaromatization to ethane or aromatic compounds [34], oxidative dehydrogenation of propane/ethane to propene/ethane [35], epoxidation of ethane [36] and anaerobic oxidation of CH₄ for methanol synthesis [37]. With CaO scavenger to remove CO₂, high-purity H₂ can be produced through sorption-enhanced steam reforming [38]. The loop is complete with

a calcinator for CaCO_3 decomposition and an oxidizer for oxygen carrier regeneration.

Figure 2.2 summarizes these typical chemical looping processes.

Although the overall change of Gibbs free energy (ΔG) of a reaction is identical to the sum of ΔG of the sub-reactions, the reaction equilibrium may be shifted with extra energy provided. For example, commercial steam reforming of CH_4 is carried out at $\sim 900^\circ\text{C}$ to produce syngas, while Vitaly L. Sushkevich and co-workers [37] reported the selective anaerobic oxidation of CH_4 to methanol over a Cu-containing zeolite with water. Researchers also commented that the CH_4 reforming with water to generate methanol and H_2 is highly unfavorable at any temperature [39]. The authors replied and showed that the surface concentrations of the reaction species and the stabilizing effect of additional water molecules fully support the feasibility of the proposed reaction [40]. Therefore, through stepwise reactions, chemical looping could benefit the circumvent of some thermodynamic limitation.

2.2 Development of oxygen carriers for chemical looping

As mentioned above, the property of the oxygen carrier is essential to the whole chemical looping system. Material chemistry and engineering offered many opportunities for the optimization of the oxygen carrier. In the early research, the selection of oxygen carrier is done by the trial and error method [41]. Up to now, hundreds of oxygen carriers have been experimentally screened. It has been shown that single metal oxide is usually not suitable oxygen carrier because the cycle stability is unsatisfactory resulting from the inevitable particle aggregation and

sintering under the harsh reaction conditions. The common oxygen carriers are comprised of the active metal oxides and the sintering-resistant support material. The active metal oxides are typically Ni, Fe, Cu, Mn, Co-based oxides or their mixture. The relative reactivity of these metal oxides with CH₄ and syngas was reported in a sequence like NiO > CuO > Mn₃O₄ > Fe₂O₃ [42]. Catalyst supports such as Al₂O₃, ZrO₂, CeO₂, SiO₂ and MgAl₂O₄ are usually used to support the active metal oxides. The support material is beneficial for increasing the dispersion of the active metal oxides, reducing the sintering effect and enhancing the mechanical properties, thus increasing the activity and cyclic stability of the oxygen carrier. It was also reported that the redox property can be tuned with reducible supports, showing the synergetic effect of metal oxides and supports [43]. However, the support also reduces the oxygen transfer capacity (OTC). Therefore, trade-off exists between the reactivity/stability and the OTC when optimizing the oxygen carrier performance and the content of active metal oxide.

Table 2.1 The summary of the preparation methods for the oxygen carriers.

Methods	Advantages	Disadvantages	Ref.
Mechanical mixing and calcination	Procedure easy to control, large scale syntheses, high yield	Large grain size, inferior dispersion uniformity	[44]
Freeze granulation	Spherical morphology of particles	High manufacturing cost	[45]
Spray drying	Large scale syntheses	Complex procedures	[46]
Sol-gel	Fine grain size, high dispersion	High cost of alkoxides precursor	[47]
Impregnation	Simple procedure	Low loading ratio	[48]
Co-precipitation	Atomic mixing of precursor	Different precipitation pH values with different metals	[49]

For the preparation of the oxygen carrier, various methods have been established, including the mechanical mixing of the component powders, freeze granulation, spray drying, sol-gel, liquid impregnation and co-precipitation. The merits and shortages of the preparation methods are summarized in Table 2.1. In this thesis, the oxygen carriers are prepared by co-precipitation to form LDH precursors, followed by calcination to obtain the mixed oxides. The LDH precursors can benefit the high surface area and the formation of equilibrium phases in the prepared oxygen carriers.

2.2.1 Ni-based oxygen carriers

Due to the good reactivity with various fuels and the excellent performance at high temperatures, Ni-based oxygen carriers have been the most widely investigated material in the chemical looping research community. The drawbacks of Ni-based oxygen carriers are the high cost and carcinogenic toxicity of Ni(II). Although there is a restriction that a small portion of CO and H₂ may be generated in the gas outlet of the fuel reactor according to the thermodynamic analysis, almost complete CH₄ conversion can be achieved by CLC using Ni [50, 51]. Ni-based oxygen carriers with Al₂O₃, ZrO₂, CeO₂ and MgAl₂O₄ have been developed and tested. In addition to the laboratory-scale investigations, Ni-based oxygen carriers have also been extensively studied in pilot prototypes, demonstrating the potential application of this type of oxygen carrier in chemical looping technology [52]. The state-of-the-art oxygen carrier is NiO particles supported on Al₂O₃. However, in NiO/Al₂O₃ oxygen carriers, NiO may react with Al₂O₃ to form NiAl₂O₄ spinel, which possesses limited reactivity

in CLC [53]. As a result, the OTC will decrease. Many efforts have been made to investigate the reactivity of NiAl_2O_4 and to avoid or reduce the interaction between NiO and Al_2O_3 . Since the formation of NiAl_2O_4 spinel is dependent on the crystal structure of Al_2O_3 supports, a simple heat treatment of $\gamma\text{-Al}_2\text{O}_3$ at $1150\text{ }^\circ\text{C}$ to form $\alpha\text{-Al}_2\text{O}_3$ will hinder the spinel generation [13]. Another reported strategy is to add the oxides of basic metals, MgO , CaO or Na_2O , to form MgAl_2O_4 , CaAl_2O_4 or NaAlO_2 spinels, inhibiting the formation of NiAl_2O_4 [54-58].

2.2.2 Cu-based oxygen carriers

Cu-based oxygen carriers have been extensively studied because of their high reactivity and high OTC, no thermodynamic restriction for complete fuel conversion, and exothermic characteristics of their reduction in fuels. The price of Cu is much lower than Ni, and Cu has less environmental concerns. The main drawback of Cu-based materials is the heavy agglomeration under high temperature in redox cycles because of the low melting point of Cu ($1085\text{ }^\circ\text{C}$) [59, 60]. To eliminate the agglomeration behavior of Cu-based oxygen carriers, it was reported that the CuO content should be lower than 20 wt.% [61]. In terms of the support, when Al_2O_3 is used, CuAl_2O_4 spinel may generate from the interaction of CuO and Al_2O_3 . However, unlike NiAl_2O_4 , CuAl_2O_4 shows excellent reactivity which is similar with CuO . In addition, ZrO_2 , TiO_2 , SiO_2 , MgAl_2O_4 , bentonite, and sepiolite have also been used as support materials. Due to the decomposition behavior of CuO at elevated temperature, Cu-based oxygen carriers have been extensively studied in CLOU process, which are

promising for the application of direct CLC of coal. This technology is especially essential to the countries where coal-fired power plants produce the main electricity resource. Because of the high temperature used in CLOU, agglomeration and defluidization are the concerns that arise in this research area. High temperature resistant Cu-based oxygen carrier was reported by Forero *et al* [62]. Stable operation was achieved with γ -Al₂O₃ as support modified with 3 wt.% NiO.

2.2.3 Fe-based oxygen carriers

There is an over 100 year history of Fe-based oxygen carrier in chemical looping processes. In 1904, iron-steam reaction was already started to be used to produce H₂ [63]. Due to its abundant, low cost and environment-friendly characters, Fe-based oxygen carriers have been investigated as attractive options for chemical looping processes. However, in CLC for complete conversion of fuel to CO₂ and H₂O, Fe₂O₃ only transforms to Fe₃O₄ because of thermodynamic restrictions, resulting in a relative low OTC compared to NiO or CuO. When Fe₃O₄ is reduced to FeO or Fe, due to the low activity of the lattice oxygen, the purity of CO₂ will decrease with the higher equilibrium concentration of CO and H₂. Usually iron oxides show high reactivity with fuels, such as CO and H₂, while the reactivity with CH₄ is much lower. Various mixed metal oxides have been proposed to integrate the merits of Fe and other metal oxides. It was reported that the addition of Ni-based oxygen carrier is effective to increase the reaction rate of the reforming reaction, achieving higher CH₄ combustion efficiency [64]. The supports used in Fe-based oxygen carriers are SiO₂,

Al_2O_3 , TiO_2 , MgAl_2O_4 , and ZrO_2 -based, *etc.* When SiO_2 is applied as support, unreactive iron silicate will form gradually in several cycles, resulting in a rapid reactivity decay [50]. Different from Ni, which can catalyze the CH_4 decomposition reaction to carbon and H_2 , low carbon deposition is observed in Fe-based oxygen carriers. In addition, there is no risk of sulphate or sulphide formation with any sulfur-containing fuels at any operating temperatures [65].

2.2.4 Mix metal oxides and perovskites

Since single metal oxide can hardly fulfill all the requirements for successful chemical looping operation, mixed metal oxides composites provide more opportunities for improvements in lowering the material costs, increasing the reactivity and thermal stability, enhancing the mechanical strength, minimizing the carbon deposition, and the usage of environmental bargain materials. Interaction of the mixed metal oxides may form new phases or bring lattice defects, offering effective ways for the manipulation of oxygen carrier activity. For example, in CLOU, Mn and Co-based oxygen carrier could spontaneously release molecular O_2 under typical fuel reforming conditions to offer high P_{O_2} , but in turn its regeneration by air is kinetically slow. Modification of Co-based oxygen carrier with Fe was reported to be effective in enhancing the oxidation kinetics, although the rate of oxygen uncoupling was reduced [66]. Yngve and co-workers investigated the Fe-Mn oxide system for CLC [67]. They found that increasing the Mn content up to 33% will result in increased reaction kinetics and capacity at lower temperature and enhanced CH_4

conversion.

Perovskite is a class of crystalline material with a general formula of ABX_3 , in which A and B are both metal cations, and the atomic radius of A is larger than that of B. A sites are usually large cations such as Ca^{2+} , Ba^{2+} , Sr^{2+} , La^{2+} , Na^+ and K^+ , *etc.* transition metals are usually located on the B sites and halides and oxides on the X sites. The A and B sites are partially substitutable by other metals with appropriate size and charge, facilitating the modification of the element components and the properties in chemical looping study. If the A or B sites are partially substituted with lower valence cations, oxygen vacancy may be created in the lattice. Due to these defects, the oxygen ion conductivity could be enhanced. Substitution of A sites with the formula of $La_{1-x}Sr_xFeO_3$ and B sites with formula of $LaMn_xFe_{1-x}O_3$ and $CaMn_xTi_{1-x}O_3$ have both been investigated, to tune the reactivity with fuels and research on the CLOU behaviors [68-70]. However, the major drawback of perovskite materials as oxygen carrier is their low OTC compare to pure oxides and high cost if rare earth metals are used.

2.2.5 Ores

For pilot scale demonstration and industrial application of chemical looping technologies, large amount of oxygen carrier materials are needed. One important requirement for the oxygen carrier is that the cost should be as low as possible. Mineral ores are proposed as a solution for the cost problem. To date, various natural ores and metal oxides from industrial residues have been tested, typically hematite,

ilmenite and red mud, in the chemical looping combustion of coal, biomass, char and CH_4 [18-20, 71]. Furthermore, in order to increase the reactivity the low cost ores, material modification has been reported effective via the integration of highly reactive NiO, Cu-based oxygen carriers, and the promotion of CeO_2 support [72-74].

Chapter 3 Techniques of Material Syntheses, Characterization, and Chemical Looping Reactions

3.1 Synthesis methodologies

In this thesis, Ni-based oxygen carriers (Ni-Mg-Al₂O₃, Ni-Cu-Al₂O₃ and Ni-Fe-Al₂O₃) were synthesized by thermal decomposition of the corresponding layered double hydroxides (LDH) precursors under air. LDH is a kind of two-dimensional layered material with relative high surface area, which is able to provide uniform mixing of cations at a molecular level, allowing the readily formation of equilibrium compositions upon the calcination at high temperatures. The LDH precursors for the oxygen carriers were prepared by a co-precipitation method, which allows scalable synthesis.

3.1.1 Materials

Nickel(II) nitrate hexahydrate Ni(NO₃)₂ 6H₂O (Sigma-Aldrich, ≥99.0%), magnesium nitrate hexahydrate Mg(NO₃)₂ 6H₂O (Sigma-Aldrich, ≥99.0%), aluminium nitrate nonahydrate Al(NO₃)₃ 9H₂O (Sigma-Aldrich, ≥98%), copper(II) nitrate trihydrate Cu(NO₃)₂ 3H₂O (Sigma-Aldrich, ≥99.0%), Iron(II) sulfate heptahydrate FeSO₄ 7H₂O (Sigma-Aldrich, ≥99.0%), urea NH₂CONH₂ (Sigma-Aldrich, ≥99.5%), sodium hydroxide NaOH (Sigma-Aldrich, ≥97%), sodium carbonate Na₂CO₃ (Sigma-Aldrich, ≥99.0%).

3.1.2 Preparation of Ni-Mg-Al₂O₃ oxygen carriers

An aqueous solution with stoichiometric amount of Ni(NO₃)₂ 6H₂O, Mg(NO₃)₂ 6H₂O and Al(NO₃)₃ 9H₂O (ratios shown in Table 3.1) was made. Calculated amount of urea was then added to achieve urea concentration of 0.5 M in the resulting reaction mixture, which was sealed and immersed in an oil bath at 90 °C for 24 h without stirring. Upon heating, urea slowly decomposed, providing a stable basic environment for the precipitation. The resulting green precipitates were filtered and washed with excess amount of deionized water. The solid product was dried at 60 °C overnight. the composite metal oxide oxygen carriers were obtained by calcining the LDH precursors in air at 1000 °C for 6 h with a heating rate of 2 °C/min. Based on the stoichiometry, the precursors are denoted as Ni₂MgAl-LDH, Ni_{2.5}Mg_{0.5}Al-LDH and Ni₃Al-LDH, with the resulting oxides denoted as Ni₂MgAl, Ni_{2.5}Mg_{0.5}Al and Ni₃Al, respectively.

Table 3.1 The preparation recipe of the Ni/Mg/Al LDH precursors with varying Ni/Mg ratios.

	Ni(NO ₃) ₂ 6H ₂ O	Mg(NO ₃) ₂ 6H ₂ O	Al(NO ₃) ₃ 9H ₂ O	urea	Oxygen carrier notation
1#	2	1	1	10	Ni ₂ MgAl
2#	2.5	0.5	1	10	Ni _{2.5} Mg _{0.5} Al
3#	3	0	1	10	Ni ₃ Al

3.1.3 Preparation of Ni-Cu-Al₂O₃ oxygen carriers

The Ni/Cu/Al LDH precursors were prepared by hydrothermal syntheses. In a typical synthesis, stoichiometric amount of Ni(NO₃)₂ 6H₂O, Cu(NO₃)₂ 3H₂O, Al(NO₃)₃ 9H₂O and urea (ratios shown in Table 3.2) were dissolved in 50 mL of deionized water in a 100 mL Teflon-lined stainless steel autoclave reactor. The concentration ratio of divalent cations (Cu²⁺ and Ni²⁺) to trivalent cations (Al³⁺) in the mixed solution was controlled at 3:1. The concentration of urea was fixed at 0.2 M. The reaction was conducted at 120 °C for 24 h. Thereafter, the resulting precipitates were extracted by centrifugation, washed with deionized water three times, and then dried in air at 65 °C overnight. The dried precipitates were ground into powders for characterization and further processing. The mixed-oxide oxygen carriers were prepared by calcining the LDH precursors in a muffle furnace at 1000 °C for 6 h in air at a heating rate of 2 °C/min.

Table 3.2 The preparation recipe for the Ni/Cu/Al LDH precursors with varying Ni/Cu ratios.

	Ni(NO ₃) ₂ 6H ₂ O	Cu(NO ₃) ₂ 3H ₂ O	Al(NO ₃) ₃ 9H ₂ O	urea	Oxygen carrier notation
1#	3	0	1	2	Ni _{1.32} Al
2#	2.5	0.5	1	2	Ni _{0.94} Cu _{0.46} Al
3#	2	1	1	2	Ni _{0.32} Cu _{0.90} Al
4#	1	2	1	2	Ni _{0.12} Cu _{0.71} Al
5#	0	3	1	2	Cu _{0.80} Al

3.1.4 Preparation of Ni-Fe-Al₂O₃ redox catalysts

Ni-Fe redox catalysts were synthesized by co-precipitation of Ni²⁺, Fe²⁺ and Al³⁺ aqueous solution with NaOH and Na₂CO₃, followed by calcination. The molar ratio of the metal salts to the alkaline was displayed in Table 3.3 with fixed ratio (at 2) of divalent cations (Ni²⁺ and Fe²⁺) to trivalent Al³⁺. In a typical synthesis, 10 mmol of divalent salts (Ni(NO₃)₂·3H₂O and FeSO₄·7H₂O) and 5 mmol of Al(NO₃)₃·9H₂O were dissolved in 12.5 mL of deionized water as solution A; 30 mmol of NaOH was dissolved in 12.5 mL of deionized water as solution B; and 6 mmol of Na₂CO₃ was dissolved in 32 mL of deionized water as solution C. For the co-precipitation, solution A and B were parallel (1 drop/s) added to solution C in a 250 mL bottle under vigorous stirring at 60 °C. The slurry was then aged at 60 °C under stirring for 24 h. Afterwards, the precipitates were washed 5 times with deionized water by centrifugation. The resulting gel was dried at 65 °C overnight and then ground into fine powders. To obtain the Ni-Fe-Al redox catalysts, the powder was calcined in a muffle furnace at 1000 °C for 6 h under air at a heating rate of 2 °C/min. The as-prepared catalysts were denoted as Ni_{2-x}Fe_xAl, where x corresponds to the Fe/Al molar ratio.

Table 3.3 A series of Ni-Fe redox catalysts prepared with varying Ni/Fe ratios.

	Ni(NO ₃) ₂ 6H ₂ O	FeSO ₄ 7H ₂ O	Al(NO ₃) ₃ 9H ₂ O	NaOH	Na ₂ CO ₃	Catalyst notation
1#	2	0	1	6	1.2	Ni ₂ Al
2#	1.5	0.5	1	6	1.2	Ni _{1.5} Fe _{0.5} Al

3#	1	1	1	6	1.2	NiFeAl
4#	1.5	0.5	1	6	1.2	Ni _{0.5} Fe _{1.5} Al
5#	0	2	1	6	1.2	Fe ₂ Al

3.2 Techniques of characterization

3.2.1 Characterization of redox catalyst morphologies and structures

The crystalline phases in the solid samples were measured using powder X-ray diffraction (XRD) on a Bruker AXS D8 diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 40 mA under ambient condition. The morphology was studied using a field emission scanning electron microscopy (JEOL JSM 6700F). The measurements of the Brunauer–Emmett–Teller (BET) specific surface area were carried out with Micromeritics ASAP Tri-star 3020 adsorption apparatus at $-196 \text{ }^{\circ}\text{C}$ up to 1 bar using the liquid nitrogen adsorption-desorption method.

The crystalline phase composition and lattice parameters of the Ni-Mg-Al₂O₃ oxygen carriers were analyzed by performing Rietveld refinement of the XRD patterns using GSAS and EXPGUI [75, 76]. To study the phase composition of the Ni-Cu-Al₂O₃ oxygen carriers before and after CLC cycles, synchrotron X-ray powder diffraction (SXRD) was performed on beamline ID22 at the European Synchrotron Radiation Facility, Grenoble, France. The SXRD was undertaken in transmission geometry with an X-ray energy of 35.0 keV. Diffractograms were collected using a 9-channel Si 111 multianalyser stage detector at a scan rate of $0.8 \text{ }^{\circ}\text{min}^{-1}$.

3.2.2 Thermogravimetric analysis (TGA)

The total amount of lattice oxygen available for chemical looping reactions, *i.e.* the mass fraction of reducible NiO in the freshly prepared Ni-Mg-Al₂O₃ oxygen carrier samples was determined by reducing the oxygen carriers in 5 vol.% H₂ (N₂ balance) in a thermogravimetric analyser (TGA/DSC2, Mettler Toledo). In each reduction, about 15 mg sample was heated to 900 °C at a heating rate of 20 °C/min and then reduced in a constant flow of 50 mL/min of 5 vol.% H₂ in N₂ for 6 h, which was found sufficient for the samples' weight loss to reach a steady-state.

The bulk compositions of the Ni-Cu-Al₂O₃ samples were determined by TGA. In a typical analysis, ~10 mg of fresh oxide sample was first degassed in N₂ at 700 °C for 120 min, followed by temperature ramp to 1100 °C in N₂ at a rate of 10 °C/min and dwell time 60 min, allowing all Cu(II) species (including those in CuO and CuAl₂O₄), to decompose to Cu(I) species (Cu₂O and CuAlO₂). The sample was subsequently exposed to 5 vol.% H₂ in N₂ at 900 °C for 180 min, to reduce all Cu(I) and Ni(II) (including those in NiO and NiAl₂O₄), to their corresponding metallic forms. Thus, the weight losses during the Cu(II) decomposition stage and the H₂ reduction stage can be used to deduce the mole fraction of Cu²⁺ and Ni²⁺ (according to Equation 3.1 & 3.2), respectively. The mole fraction of Al³⁺ is then determined by oxygen balance.

$$x_{\text{CuO}}(\text{wt}\%) = \frac{(m_{\text{max}} - m_{\text{min,OU}}) * M_{\text{CuO}} * 2}{M_{\text{O}} * m_{\text{max}}} * 100 \quad (3.1)$$

$$x_{\text{NiO}}(\text{wt}\%) = \frac{((m_{\text{max}} - m_{\text{min,re}}) - 2 * (m_{\text{max}} - m_{\text{min,OU}})) * M_{\text{NiO}}}{M_{\text{O}} * m_{\text{max}}} * 100 \quad (3.2)$$

where $m_{\max}$ is the sample mass after stabilization at 700 °C under N₂ for 120 min; $m_{\min,OU}$ and $m_{\min,re}$ are the sample mass at the end of the Cu(II) decomposition and H₂ reduction of Cu(I) and Ni(II); M_O , M_{CuO} and M_{NiO} are the corresponding molar mass, respectively.

The qualitative analysis of the lattice oxygen activities of the Ni-Cu-Al₂O₃ oxygen carriers were performed by temperature programmed reduction (TPR) using the same TGA with the following program: (i) oxidation in air at 800 °C for 60 min, (ii) an isotherm in N₂ at 100 °C for 10 min, (iii) temperature ramp from 100 °C to 1000 °C at a rate of 5 °C/min in 5 vol.% H₂ in N₂.

TPR with H₂ and TPO with CO₂ were performed in sequence for the Ni-Fe-Al₂O₃ samples. Freshly prepared Ni-Fe redox catalysts were loaded into the TGA cell filled with N₂ flow (40 mL/min). Before reduction, ~10 mg of the catalyst was heated up to 900 °C at a ramp rate of 20 °C/min and held for 60 min under air (60 mL/min) to ensure its full oxidation. After cooling down to 100 °C, TPR was carried out at a ramp rate of 10 °C/min up to 1100 °C under 5 vol.% H₂/N₂ (60 mL/min). The reduced sample was then cooled to 100 °C in the same reducing atmosphere, which was subsequently switched to CO₂ (60 mL/min) for the TPO up to 1100 °C at a ramp rate of 10 °C/min. The first derivative of the mass change was obtained from the built-in software to validate the reduction/oxidation peaks. Solid conversion during TPR and TPO were calculated based on:

$$X = (m_{ox} - m)/(m_{ox} - m_{re}) \quad (3.3)$$

where m_{ox} and m_{re} are the mass of the Ni-Fe redox catalyst before and after reduction, respectively, and m is the instantaneous sample mass during the reduction and oxidation.

3.2.3 H_2 -TPR in CATLAB

The reactivity of the lattice oxygen in the Ni-Mg- Al_2O_3 oxygen carriers, before and after cycling, was characterized by H_2 -TPR using a commercial microreactor system (CATLAB, Hiden Analytical). During H_2 -TPR, 10 mg of the oxygen carriers were degassed at 200 °C in 50 mL/min (STP) of Ar and heated to 900 °C at 10 °C/min in 50 mL/min (STP) of 5 vol.% H_2 (balance N_2). The H_2 -TPR profiles, *viz.* the mass spectrometer signals of H_2 and H_2O in the off-gas, were measured by an online mass spectrometer (QGA, Hiden Analytical).

3.3 Chemical looping reactions

The prepared oxygen carriers were subjected to redox cycles in a fixed bed by feeding reducing and oxidizing gases in an alternating sequence. Figure 3.1 shows the Schematic of experimental set-up. The tubular fixed bed reactor is made of recrystallized alumina with I.D. of 9 mm. The packing arrangement in the fixed bed, from top to bottom, is as follows: 9.0 g of white Al_2O_3 sand (1400–1700 μm), 0.1 g of oxygen carrier (powder), 2.0 g of white Al_2O_3 sand (300–425 μm), 5.8 g of white Al_2O_3 sand (1400–1700 μm) and silica wool. Such packing ensures that the active bed, *viz.* the oxygen carrier, is at the centre of the heated zone where the temperature profile can be approximated as uniform.

For the Ni-Mg-Al₂O₃ samples, redox cycles were undertaken isothermally at 800 °C with reduction in 5 vol.% H₂ (N₂ balance) and oxidation in 5 vol.% O₂ (N₂ balance), respectively. The reduction and oxidation both last 5 minutes, with a 2 min N₂ purge period in between. The volumetric flowrates of the gases were kept at 225 mL/min (STP) for all stages of the cycling experiments using mass flow controllers. The composition of the effluent gas was measured using online gas analysers (Caldos 27 and Magnos 206, EL 3020, ABB) at a sampling frequency of 1 Hz.

Figure 3.1 Schematic of experimental set-up for the chemical looping study.

For the Ni-Cu-Al₂O₃ samples, in each redox cycle, the feed gases were, in consecutive order: 1 min of N₂, 5 min of 5 vol.% CH₄ in N₂, 1 min of N₂, and 5 min of 5 vol.% O₂ in N₂. The cycling experiments were conducted isothermally at 800 °C, whilst the gas flow rate was maintained at 225 mL/min.

The Ni-Fe-Al₂O₃ redox catalysts were investigated for steam reforming of CH₄ to make syngas at 900 °C. Redox cycles were performed isothermally with 3 gas stages (5 min each): 5 vol.% CH₄/N₂ reduction (stage I), steam oxidation (stage II) and 5 vol.% O₂/N₂ oxidation (stage III). Pure N₂ was used to purge the reactor for 2 min between different stages and as the carrier gas in stage II. The volumetric flow rate of the gases were measured and controlled using mass flow controllers, at ~110 mL/min (STP) for all stages of the cycling experiments, and 10 µL/min of water was introduced into the bed with a Shimadzu HPLC pump (LC-20AT) during stage II. Using a condensing tube and a U type tube filled with CaCl₂ beads to remove water vapor, the composition of the dry effluent gas mixture was measured using online gas analyzers (Caldos27 and Magnos206 EL3020, ABB) at a frequency of 1 Hz. After 30 cyclic experiments at 900 °C, redox cycles were also performed at 700, 750, 800, 850 and 900 °C to investigate the temperature effect on the performance, with 5 cycles for each temperature. CLSRM cycles without stage III were also performed to study the effect of catalyst regeneration with O₂. To compare the performance of looping reforming with traditional steam reforming of CH₄, co-feeding of 5 vol.% CH₄/N₂ and 10 µL/min of water (stacking stages I and II) into the active bed was also conducted, followed by 5 vol.% O₂/N₂ oxidation (stage III). The schematic of the three CLSRM processes were shown in Figure 3.2.

Figure 3.2 Illustration of chemical looping steam reforming of methane (CLSRM) processes. (a) CLSRM with O₂ regeneration, (b) without O₂ regeneration, and (c) co-feeding reforming.

3.4 Result analysis

During the cycling experiments of the Ni-Mg-Al₂O₃ oxygen carrier in the fixed bed, the amounts of lattice oxygen transferred during reduction and oxidation, $N_{O,red}$ and $N_{O,ox}$, are calculated based on the number of moles of H₂ and O₂ consumed by the active bed during the reduction phase and the oxidation phase, respectively:

$$N_{O,red} = N_{H_2,red} = \int_0^{t_{max}} (y_{H_2} - y_{H_2,blank}) \dot{N} dt \quad (3.4)$$

$$N_{O,ox} = 2N_{O_2,ox} = 2 \int_0^{t_{max}} (y_{O_2} - y_{O_2,blank}) \dot{N} dt \quad (3.5)$$

where y_{H_2} and y_{O_2} are the gas mole fractions of H_2 and O_2 leaving an inert bed of almost identical packing arrangement, respectively; $y_{H_2,blank}$ and $y_{O_2,blank}$ are the gas mole fractions of H_2 and O_2 leaving an active bed, respectively. $\dot{N}$ is the gas molar flowrate through the fixed bed and t_{max} (300 s) is the total duration of the reduction or the oxidation stage. Thus, fractional conversion, X , of NiO to Ni during reduction, can be calculated using a mass balance of the amount of H_2 consumed during reduction:

$$X = \frac{N_{O,red(ox)} M_{NiO}}{m_0 x_{NiO}} \quad (3.6)$$

where m_0 is the mass of the fully oxidised sample, M_{NiO} is the molecular mass of NiO and x_{NiO} is the mass fraction of NiO in the fully oxidised sample, assuming the oxygen carriers consist of only unary oxides, *i.e.* NiO, MgO and Al_2O_3 . From this point onwards, X is used as a measure of a material's ability to carry oxygen.

For the Ni-Cu- Al_2O_3 and Ni-Fe- Al_2O_3 oxygen carriers, blank test was performed to determine the amount of CH_4 and O_2 introduced during the 5 min 5 vol.% CH_4 reduction and 5 vol.% O_2 oxidation, which were calculated as:

$$N_{CH_4,in} = \int_0^{t_{max}} y_{CH_4,blank} * \dot{N} dt \quad (3.7)$$

$$N_{O_2,in} = \int_0^{t_{max}} y_{O_2,blank} * \dot{N} dt \quad (3.8)$$

Since total gas flow rate would fluctuate as a result of the gas-solid reaction, N_2 was used as the standard to determine the total flow rate ($mmol\ s^{-1}$):

$$\dot{N}_{re} = \dot{N}_{N_2,re}/(1 - \sum y_i) \quad (3.9)$$

$$\dot{N}_{ox,O_2} = \dot{N}_{N_2,ox,O_2}/(1 - \sum y_j) \quad (3.10)$$

where y_i and y_j are the molar fraction of each component i (CH_4 , CO_2 , CO and H_2) in the reduction, and component j (CO_2 , O_2) in the O_2 oxidation. The amount of each component (mmol) out of the bed was then calculated as:

$$N_i = \int_0^{t_{max}} y_i * \dot{N}_{re} dt \quad (3.11)$$

$$N_j = \int_0^{t_{max}} y_j * \dot{N}_{ox,O_2} dt \quad (3.12)$$

The amount of carbon deposited (mmol) in 5 vol.% CH_4 reduction was estimated by adding the amount of CO_2 and CO generated during the oxidation stage.

$$N_{carbon} = \int_0^{t_{max}} (y_{CO_2,ox} + y_{CO,ox}) \dot{N} dt \quad (3.13)$$

CH_4 conversion during reduction was calculated as:

$$X_{CH_4} = (N_{CH_4,in} - N_{CH_4})/N_{CH_4,in} \quad (3.14)$$

The selectivity of component i (CO_2 , CO and carbon deposition) and H_2 during 5 vol.% CH_4 reduction were calculated by:

$$S_i = N_i/(N_{CO_2,re} + N_{CO,re} + N_{carbon}) \quad (3.15)$$

$$S_{H_2} = 0.5 * N_{H_2,re}/(N_{CO_2,re} + N_{CO,re} + N_{carbon}) \quad (3.16)$$

The oxygen carrier conversion during reduction with 5 vol.% CH₄ was calculated by:

$$X_{\text{reduction}} = \frac{(N_{\text{CO}_2,\text{re}} * 4 + N_{\text{CO},\text{re}}) * M_{\text{MeO}}}{m_0 x_{\text{MeO}}} \quad (3.17)$$

where m_0 is the sample mass; x_{MeO} (mass fraction of Ni/Cu oxides) was calculated from the fraction of NiO and CuO determined by TGA; and M_{MeO} (average molar mass) is the arithmetic average of M_{NiO} and M_{CuO} considering their mole fraction in the oxygen carrier.

$$x_{\text{MeO}} = x_{\text{CuO}} + x_{\text{NiO}} \quad (3.18)$$

$$M_{\text{MeO}} = \frac{x_{\text{MeO}}}{x_{\text{CuO}}/79.5 + x_{\text{NiO}}/74.7} \quad (3.19)$$

For CLSRM process, similar calculation for the CH₄ conversion and selectivities was applied. During the steam oxidation stage, the total flow rate was calculated using N₂ as the standard, and amount of component k (H₂, CO₂, CO) were calculated by:

$$\dot{N}_{\text{ox,steam}} = \dot{N}_{\text{N}_2,\text{ox,steam}} / (1 - \sum y_k) \quad (3.20)$$

$$N_k = \int_0^{t_{\text{max}}} y_k * \dot{N}_{\text{ox,steam}} dt \quad (3.21)$$

The amount of gases was normalized by catalyst mass to calculate the corresponding productivity (mol kg⁻¹). The conversion of steam was calculated by:

$$X_{\text{steam}} = N_{\text{H}_2,\text{ox,steam}} * 18/50 \quad (3.22)$$

The oxygen carrier conversion during the 3 reaction stages were calculated by:

$$X_{re} = (N_{CO_2,re} * 4 + N_{CO,re})/O\_mmol \quad (3.23)$$

$$X_{ox,steam} = (N_{H_2,ox,steam} - N_{CO_2,ox,steam} * 2 - N_{CO,ox,steam})/O\_mmol \quad (3.24)$$

$$X_{ox,O_2} = (N_{O_2,in} - N_{O_2} - N_{CO_2,ox,O_2}) * 2/O\_mmol \quad (3.25)$$

where O_mmol is the theoretical amount of available oxygen (mmol) in the Ni-Fe redox catalyst, which is calculated as:

$$O\_mmol = mass * x_{NiO}/100/M_{NiO} + mass * x_{Fe_2O_3}/100/M_{Fe_2O_3} \quad (3.26)$$

Chapter 4 Phase Interactions in NiO-MgO-Al₂O₃ Oxygen Carriers over H₂ Reduction and O₂ Oxidation Looping Cycles

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4.1 Introduction

CCS is a mid-term strategy to mitigate anthropogenic CO₂ emission in order to combat climate change. The capture of CO₂ is responsible for the majority of the cost associated with CCS. As an innovative fuel conversion technology with inherent CO₂ separation, CLC offers the advantage of negligible energy penalty compared to conventional carbon capture processes such as amine scrubbing or cryogenic gas separation [3, 5, 7, 8]. In a typical CLC process, the air-combustion of fuel is divided into two sub-reactions. Firstly, the fuel reacts with lattice oxygen from an oxygen carrier, producing only CO₂ and steam. After removing the steam by condensation, a pure stream of CO₂ can be readily sequestered. To close the loop, the reduced oxygen carrier reacts with air to recover to its original oxidation state. In addition, the chemical looping concept can be adapted for H₂ production, CH₄ reforming and gasification using water or CO₂ as feedstock [11, 28, 77].

Apart from the process and reactor design, the development of oxygen carriers is vital to chemical looping operations. Criteria for choosing ideal oxygen carriers include (i) high lattice oxygen reactivity, (ii) high oxygen carrying capacity, (iii) stable performance over prolonged cycling and (iv) good mechanical strength if

applied in fluidized beds. In order to lower the cost of the oxygen carrier, mineral ores were investigated both in laboratory and pilot scales [18-20, 67, 72, 78, 79]. However, the optimisation of the reactivity and cyclic stability of ores is limited due to their complex and non-uniform compositions. Therefore, the development of suitable synthetic oxygen carriers with well-defined structures and compositions for high reactivity and cycle stability at reasonable costs is still attractive to the advancement of chemical looping technologies. Typically, the oxides of first-row transition metals, *viz.* Mn, Fe, Co, Ni and Cu are good candidates for synthetic oxygen carriers because they match criteria (i) and (ii) above [11, 13]. To satisfy criteria (iii) and (iv), the active metal oxides are supported on common catalyst supports such as Al_2O_3 , SiO_2 , ZrO_2 , TiO_2 , CeO_2 and MgAl_2O_4 . However, under the operating conditions for CLC, *i.e.* 800 - 1000 °C, the formation of low reactivity aluminate spinel compounds *e.g.* NiAl_2O_4 , CuAl_2O_4 , FeAl_2O_4 , undermines the performance of the oxygen carriers [55, 59, 80-82]. To mitigate the undesirable spinel formation whilst exploiting the low-cost Al_2O_3 support, researchers proposed to add stoichiometric amount of basic metal oxides such as MgO, CaO or Na_2O , which form more stable spinels such as MgAl_2O_4 , CaAl_2O_4 or NaAlO_2 , to inhibit the Al_2O_3 from reacting with the transition metal oxides [54, 56, 58, 60]. However, this approach overlooks the possible formation of solid solutions of aluminates. For example, a recent study suggested that adding excessive amount of Na_2O to a $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ mixture could not inhibit FeAlO_2 , owing to the formation of a NaFeO_2 - NaAlO_2 solid solution [83], which compromises the inertness of NaAlO_2 .

The present study investigates the role of MgO in inhibiting the Ni-Al-O interaction and its implication to the formulation of oxygen carriers for CLC. Despite multiple reports of MgAl_2O_4 being assumed and used as an inert support for NiO based oxygen carriers [84-87], it is still unclear how much NiAl_2O_4 can be irreversibly replaced by MgAl_2O_4 , since MgO - NiO, and MgAl_2O_4 - NiAl_2O_4 can form a halite phase solid solution and a spinel phase solid solution, respectively [52, 57, 88]. In addition, we report a recipe to prepare oxygen carriers from Mg/Ni/Al layered double hydroxides (LDH). LDH is chosen as the precursor not only because it possesses the unique nano-plate structure with relatively high surface area, but also because it provides uniform mixing of cations at a molecular level, allowing the readily formation of mixed oxides and solid solution phases. Furthermore, the scale up of the synthesis is possible with a simple urea-assisted precipitation method, which does not require the use of sodium salts precipitants such as sodium hydroxide and sodium carbonate, eliminating any potential contamination of the oxygen carrier by sodium.

4.2 Results and discussion

4.2.1 Materials characterization

Typical morphologies of the co-precipitated precursors and the freshly-calcined oxygen carriers were depicted in Figure 4.1. Figure 4.1 (a-c) show that the longitudinal dimension of the plates is in the range of 0.5~1 μm , with the thickness of around 40 nm. It is apparent that the plate morphology was retained after heat treatment at 1000 $^{\circ}\text{C}$ for 6 h, suggesting good thermal stability of the physical

structure of the fresh oxygen carriers. Such morphology is expected to provide sufficient surface area to facilitate rapid transport of oxygen between the solid and the gas phase. X-ray diffraction (XRD) patterns of the as-prepared precipitates, shown in Figure 4.2, suggests a single LDH phase generated with no other impurity, indicating the successful synthesis of LDH from the urea-assisted precipitation. Accordingly, the BET surface areas of the samples, shown in Table 4.1 (N_2 absorption and desorption isotherms are shown in Figure 4.3), indicate that the high surface areas of the LDH precursors have been preserved after the thermal treatment at 1000 °C, exceeding 40 m^2/g in all three formulations. However, these numbers dropped significantly after 100 redox cycles.

Figure 4.1 SEM images of the LDH precursors (a-c), fresh oxygen carriers calcined at 1000 °C for 6 h (d-f) and the spent oxygen carriers after 100 redox cycles (g-i). Images a)-i) were taken at the same magnification, so as the inserts in images a)-c).

Figure 4.2 XRD patterns of $\text{Ni}_{3-x}\text{Mg}_x\text{Al}$ LDH precursors: (a) $\text{Ni}_2\text{MgAl-LDH}$, (b) $\text{Ni}_{2.5}\text{Mg}_{0.5}\text{Al-LDH}$ and (c) $\text{Ni}_3\text{Al-LDH}$.

Figure 4.3 N_2 adsorption and desorption isotherms of the LDH precursors (a-c), fresh (d-f) and spent (g-i) oxygen carriers after 100 chemical looping cycles.

Table 4.1 The measured BET surface area of the NiMgAl LDH precursors, fresh oxygen carriers calcined at 1000 °C for 6 h, and the spent oxygen carriers after 100 redox cycles.

Sample	BET surface area (m ² /g)		
	Ni ₂ MgAl	Ni _{2.5} Mg _{0.5} Al	Ni ₃ Al
LDH precursors	60.0	52.5	62.4
Fresh oxygen carriers	60.9	47.1	40.3
Spent oxygen carriers	17.1	6.8	4.6

Figure 4.4 The reduction curve of the fresh NiO-MgO-Al₂O₃ oxygen carriers under 5 vol.% H₂/N₂ at 900 °C in TGA.

Table 4.2 The oxygen transfer capacities and NiO content in the oxygen carriers.

Sample	Oxygen transfer capacity (wt.%)		NiO content (wt.%)	
	Measured	Theoretical	Measured	Theoretical
Ni₂MgAl	14.0	13.3	65.6	62.2
Ni_{2.5}Mg_{0.5}Al	16.3	15.5	75.9	72.5
Ni₃Al	17.4	17.5	81.4	81.5

The practical availability of lattice oxygen can be deduced from the reduction experiments at 900 °C in the TGA, as shown in Figure 4.4, with the calculated results tabulated in Table 4.2. From Table 4.2, it can be seen that, the measured oxygen carrying capacity for Ni₃Al is almost identical to the values expected. However, for Ni₂MgAl and Ni_{2.5}Mg_{0.5}Al, the measured Ni contents are higher than the theoretical ones, owing to the amphoteric nature of Mg(OH)₂, which has a relatively high K_{sp} value of 5.61×10^{-12} (*cf.* that of Ni(OH)₂ of 5.48×10^{-16} and that of Al(OH)₃ of 3×10^{-32}). As a result, the partial precipitation of Mg gave rise to the increase in the Ni contents. Another noticeable feature in Figure 4.4 is the increase in the time taken for the reduction to go to completion with increasing amount of Mg²⁺. Given the large time scale used for the reactions, this trend cannot be explained by the small differences in the initial mass of the samples used or by mass transfer effects. The slower rates must therefore be attributed to the chemical inertness induced by the inclusion of Mg²⁺ in the fresh oxygen carriers. This also means that the lowest oxygen carrying capacity is expected for Ni₂MgAl under realistic chemical looping conditions.

4.2.2 Oxygen carrier performance

The calculated NiO conversions, X , for all three samples over 100 redox cycles, are shown in Figure 4.5(a). In all cases, the NiO conversions calculated from H_2 reduction and O_2 oxidation are in excellent agreement (within 2% error). For Ni_2MgAl , the NiO conversion increased sharply in the first 10 cycles from 53.9% to 72.4%, followed by gradual increments over the subsequent cycles, reaching towards 80% by the 70th cycle. The conversion of $Ni_{2.5}Mg_{0.5}Al$ increased over the initial few cycles, followed by a slow decline which stabilises at around 87%. Ni_3Al showed consistent performance over the 100 cycles with the value of NiO conversion staying between 86%-88% after a drop from 89.2% in the first cycle. To analyze the contribution of reaction rates to the variation in NiO conversion and consequently oxygen carrying capacity over cycles, the times taken to reach 60% conversion, as an indicative parameter reflecting the rates, are plotted versus cycle number in Figure 4.5(b). Additionally, the conversion versus reaction time profiles, for the 1st, 10th, 50th and 100th cycles, are shown in Figure 4.6. From Figure 4.5(a), it can be seen that, the initially slow reduction rates of Ni_2MgAl , as shown by the long time taken to reach 60% conversion, is in agreement with the slow reduction seen in the TGA reduction experiments. Over cycles, the reduction of Ni_2MgAl becomes increasingly faster, overtaking $Ni_{2.5}Mg_{0.5}Al$ and Ni_3Al by the 30th cycle. This increase in reduction rate is responsible for the improvement in CLC performance seen in Figure 4.5(a). During oxidation, the ability of reduced Ni_2MgAl to take up gaseous oxygen is the best of all three samples but decayed slowly over cycles. $Ni_{2.5}Mg_{0.5}Al$ and Ni_3Al showed

consistent reactivity during reduction but became notably more difficult to oxidize in 5 vol.% O₂/N₂. The diminished BET surface area is one of the factors responsible for the decayed reactivity during oxidation for all three samples. In addition, inter-phase and intra-phase interactions may be responsible for the changes in the reaction rates. The chemical contribution to the change in behaviour of the oxygen carriers will be discussed in the section below.

Figure 4.5 (a) The conversion of the oxygen carriers in 100 chemical looping cycles.

(b) Time taken to reach 60% oxygen carrier conversion during reduction and oxidation.

Figure 4.6 The reaction curves of the chemical looping reactions in the 1st, 10th, 50th and 100th cycle: (a-c) 5 vol.% H₂ reduction, (d-f) 5 vol.% O₂ oxidation.

Figure 4.2(g-i) show the SEM images of the cycled oxygen carriers. Although the plate structure due to the growth of LDH crystallites was preserved after calcination at 1000 °C, it did not survive 100 cycles of CLC operation at 800 °C over 23.3 h. It can be seen that the morphologies of cycled samples consist of a mixture of fine grains with a diameter *ca.* 100 nm and coarser grains with diameters *ca.* 300-500 nm, probably a product of sintering of the fine grains. It appears that the coarse grains are

most abundant in the spent Ni_3Al , which contains no Mg, and least abundant in Ni_2MgAl , which contains the most Mg. This observation is in good agreement with the change in BET surface area of the three samples, of which the surface area of Ni_3Al shrank the most, by almost 90%, whereas Ni_2MgAl and $\text{Ni}_{2.5}\text{Mg}_{0.5}\text{Al}$ retained 28% and 14% of the surface area of the fresh oxygen carriers, respectively. Although the decrease in surface area is a common phenomenon in chemical looping processes, the BET surface areas of the cycled materials in the present study are still larger than the typical $1 \text{ m}^2/\text{g}$ found in the literature [53]. Both the SEM and BET results suggest a positive correlation between the amount of Mg present and the morphological stability of the oxygen carriers. However, good structure stability and high surface area does not necessarily mean good reactivity, as material chemistry also plays an important role in determining the performance of oxygen carriers. In order to investigate the chemical changes involved during the redox cycles, the phase composition of the oxygen carriers are analyzed by XRD. The XRD patterns of oxygen carriers before and after 100 redox cycles are shown in Figure 4.7. It can be seen that the peak width decreased while the peak intensity increased after cycling, suggesting the enhanced crystallinity from sintering. This is in agreement with the presence of morphological changes observed by SEM. The refined XRD patterns, shown in Figure 4.8, suggest that for all three samples, with or without Mg^{2+} , only two phases are present – a halite phase and a spinel phase. This means that, when fully oxidized, for the fresh and spent oxygen carriers, the MgO and NiO form a solid solution whilst MgAl_2O_4 and NiAl_2O_4 form another solid solution.

Figure 4.7 XRD patterns of the fresh and spent oxygen carriers before and after 100 redox cycles. The halite and spinel phases are labelled with † and ‡, respectively.

Table 4.3 Lattice parameters of the halite and the spinel phases calculated from XRD refinements. The lattice parameters for MgO, NiO, MgAl₂O₄ and NiAl₂O₄ are 8.4224, 8.3542, 8.0831 and 8.048, respectively.

Sample	Fresh		Spent	
	Halite (Å)	Spinel (Å)	Halite (Å)	Spinel (Å)
Ni ₂ MgAl	8.363468	8.075932	8.358769	8.080112
Ni _{2.5} Mg _{0.5} Al	8.36052	8.060122	8.3563	8.065479
Ni ₃ Al	8.356344	8.052638	8.355873	8.038876

Figure 4.8 XRD patterns and refinements of the oxygen carriers before (a-c) and after (d-f) 100 redox cycles. In a), the halite and spinel phases are labelled with † and ‡, respectively.

Figure 4.9 XRD patterns and refinements of the oxygen carriers before (a-c) and after (d-f) 100 redox cycles, with CaCO_3 (calcite) as an internal standard. In a), the halite, spinel and calcite phases are labelled with †, ‡ and §, respectively.

Figure 4.10 H₂-TPR profiles of (a) the fresh samples calcined at 1000 °C for 6 h, and (b) spent samples after 100 chemical looping cycles.

4.2.3 Change in phase compositions

To explore qualitatively the composition of the two phases in each sample, XRD measurements were repeated with CaCO₃ (calcite) as an internal standard to calibrate for displacement errors. The XRD patterns with internal calibration were shown in Figure 4.9. The lattice parameters calculated from the calibrated refinement are shown in Table 4.3. From Table 4.3 it can be seen that, for Ni₂MgAl and Ni_{2.5}Mg_{0.5}Al, the lattice parameter for the halite phase is between that of MgO and NiO, whereas the lattice parameter for the spinel phase is between that of MgAl₂O₄ and NiAl₂O₄,

meaning that both phases are mixtures of Mg^{2+} and Ni^{2+} . However, both the cycled Ni_2MgAl and $\text{Ni}_{2.5}\text{Mg}_{0.5}\text{Al}$ show decrease in the cell volume for the halite phase and increase in cell volume for the spinel phase after cycling, meaning that the cycled oxygen carriers contains more Ni^{2+} in the halite phase solid solution and more Mg^{2+} in the spinel phase solid solution. In other words, redox cycling altered the phase compositions of the samples, with a net migration of Ni^{2+} from the spinel phase to the halite phase, balanced by a net migration of Mg^{2+} in the opposite direction. Similar observation has been mentioned by Mattison *et al.* [51], despite the lack of experimental data. For Ni_3Al , the refinement results also suggest changes in cell parameter, in particular, a shrinkage of the spinel phase. This phenomena may be explained by the partial depletion of Ni^{2+} ions in NiAl_2O_4 to form $\text{Ni}_{1-x}\text{Al}_{2+y}\text{O}_4$, as suggested by the equilibrium phase diagram measurement by Philips *et al.* [89].

The chemical composition of the oxides phases is also reflected by the H_2 -TPR profiles, shown in Figure 4.10. Figure 4.10(a) shows that, for the fresh $\text{Ni}_{2.5}\text{Mg}_{0.5}\text{Al}$ and Ni_3Al , there are a peak between 400 and 500 °C (α) and a peak between 800 and 900 °C (β), which correspond to the reduction of Ni^{2+} in the halite phase and the spinel phase, respectively. However, for Ni_2MgAl , there is only one peak corresponding to reduction of Ni^{2+} in the halite phase and the reduction of Ni^{2+} in the spinel phase wasn't observed. Additionally, the position of the α peak shifts to the right with more Mg^{2+} , suggesting that Ni^{2+} in the halite phase are harder to reduce with more Mg^{2+} . There is no analogous trend for the reducibility of the Ni^{2+} in the spinel phase. After 100 cycles, all three samples show two peaks at *ca.* 400 °C (α_1')

and 550 °C (α_2'). These two peaks are believed to correspond to two types of lattice oxygen in the halite phase with weak and median interaction with Al_2O_3 , an indication of phase segregation over cycling. At the same time, the positions of the β peaks shift to the right compared to that of the fresh samples, suggesting the reduced availability of the lattice oxygen in the spinel phase.

All three oxygen carriers showed good oxygen carrying capacities, as indicated by the >79% NiO conversions at the 100th cycle, as summarised in Table 4.4. From Table 2, it can be seen that, the BET surface areas of the samples rarely changed when the LDH precursors were calcined at 1000 °C for 6 hours, whereas cycling at 800 °C reduced the surface area by almost 90%. The addition of Mg^{2+} appeared to have reduced the extent of sintering. However, the high residual reactivity of Ni_3Al after 100 cycles suggest that in general synthesizing oxygen carriers from LDH precursors is a plausible approach, because the plate structure provides an initial surface area large enough to make sintering a negligible factor in determining the performance of the oxygen carrier over large number of redox cycles.

Table 4.4 Oxygen transfer capacity at the 100th cycle.

Oxygen carrier	Oxygen transfer capacity in different units		
	Solid conversion / %	mmol O/g	wt. %
Ni_2MgAl	79.0	6.6	10.5
$\text{Ni}_{2.5}\text{Mg}_{0.5}\text{Al}$	87.4	8.4	13.5
Ni_3Al	87.1	9.5	15.2

Despite the decrease in BET surface area with redox cycles, the performance of Ni₂MgAl increased. This increase can be correlated to the changes in phase compositions of the oxygen carriers measured by XRD and TPR, *i.e.* material chemistry plays an important role in determining the performance of the oxygen carriers during the redox experiments. Based on the divalent to trivalent cation ratio of 3:1 in the LDH precursors, about 83% of the divalent cations are in the halite phase, the Ni(II) in which is more reducible than that in the spinel phase, as shown by the H₂-TPR profiles shown in Figure 4.10. However, owing to the formation of the NiO-MgO solid solution, NiO becomes harder to reduce with increased of MgO content [90]. This effect is more profound in the fresh Ni₂MgAl and Ni_{2.5}Mg_{0.5}Al, because the thermal treatment at 1000 °C allowed both phases to form equilibrium solid solutions. This may also be the case that the Ni(II) in the spinel phase has reduced activity in the presence of Mg. However, the activity of the Ni(II) in the spinel phase has little impact on the overall performance of the oxygen carriers because there is relatively little spinel phase compared to the halite phase.

Given the experimental evidence, a mechanism is postulated to explain the evolution in behaviour of the oxygen carriers, as illustrated in Figure 4.11. During reduction in 5 vol.% H₂ at 800 °C, Ni²⁺ precipitates from the halite phase to form metallic Ni. This generates a concentration gradient for Ni²⁺, causing Ni²⁺ in the spinel phase to slowly migrate to the halite phase, balanced by a counter flow of Mg²⁺, resulting an increase in the activity of NiO in the halite phase over cycles. During oxidation, metallic Ni reforms NiO. However, the low ionic mobility of Ni²⁺ at

800 °C means that the regenerated NiO did not have sufficient time re-dissolve in the spinel solid solution before the start of the reduction stage in the subsequent cycle. Thus, there is an overall segregation of Ni^{2+} from the spinel phase. In addition, the XRD measurements suggest that a net flux of Ni^{2+} from the spinel phase to the halite phase also took place in Ni_3Al , as the lattice parameter of the spinel phase decreased after 100 redox cycles owing to the partial depletion of NiO in NiAl_2O_4 .

Figure 4.11 Schematic of the mechanism driving the change in phase composition during reduction of the Mg-Ni-Al-O oxygen carriers.

Figure 4.12 Solid conversion versus cycle number for Ni_2MgAl over 100 cycles at 800 °C. After 70 redox cycles, the sample was calcined in N_2 at 800 °C for 8 h before starting the 71st cycle.

An additional experiment was performed to verify the mechanism proposed in Figure 4.11. Initially, the fresh oxygen carrier Ni_2MgAl was cycled for 70 times at 800 °C, then the cycling was halted by an 8 h nitrogen purge at 800 °C resumption. The resulting variation in oxygen carrier conversion, depicted in Figure 4.12, shows that the behaviour of the oxygen carrier for the first 70 cycles repeats that seen in Figure 4.5(a), as the halite phase becomes increasingly enriched of Ni(II) and hence more reducible. However, the 8 h thermal treatment without redox reactions allowed the oxygen carrier to “anneal” and re-equilibrate to well-mixed solid solutions, making the oxygen carrier much less reactive in the 71st cycle compared to cycle 70. Further redox cycling re-activated the oxygen carriers in the same manner as the first 10 cycles. This result supports the discussion above, that the thermodynamically stable state of Ni_2MgAl is less reactive; but it can be activated by a few redox cycles.

4.2.4 Implications

So far, the experimental results suggest that, thermodynamically, Mg^{2+} will co-exist with Ni^{2+} in both the halite phase and the spinel phase. Even when the Mg:Al ratio is 1:2 (*i.e.* in the case of $\text{Ni}_{2.5}\text{Mg}_{0.5}\text{Al}$), which had been thought to correspond to a stable MgAl_2O_4 phase, Mg^{2+} is present in both phases in the fresh and the cycled sample. This disproves the assumption that an inert MgAl_2O_4 spinel can be used as a support for NiO oxygen carriers. Analogous findings were reported by Imtiaz *et al.* [91] and Liu *et al.* [83], who showed that, over chemical looping cycles, the supposedly inert MgAl_2O_4 and NaAlO_2 were in fact contaminated by Fe(III), forming $\text{MgFe}_{1.4}\text{Al}_{0.6}\text{O}_4$,

and $\text{NaFe}_{1-x}\text{Al}_x\text{O}_2$, respectively. Nevertheless, adding MgO is beneficial to the sintering resistance of the oxygen carriers over redox cycles. Furthermore, one could overcome the problem of the formation of unreactive solid solutions by pre-activating the Ni-Mg- Al_2O_3 oxygen carriers over a few redox cycles to extract the MgO from the active, NiO-rich halite phase. This approach may be useful for chemical looping operations at higher temperatures, when the formation of solution becomes unavoidable as solid diffusion becomes much faster. It would also be interesting to explore similar effects in analogous oxide systems, such as that of MgAl_2O_4 supported, CuO oxygen carriers.

In the present study, the chemical looping cycles were performed in a fixed bed reactor, where the bulk mechanical properties of the solid play little roles in determining the performance of the oxygen carrier. For applications in a circulating fluidized bed system, the bulk mechanical properties of the oxygen carriers (*e.g.* the resistance to attrition) should be optimized.

4.3 Summary

NiO based, MgO modified and Al_2O_3 supported oxygen carriers were synthesized from LDH precursors for chemical looping applications. The LDH precursors provide the oxygen carriers with initial surface areas large enough to prevent sintering from affecting their performance. The molecular level mixing in the LDH precursors also ensured the formation of halite and spinel solid solutions ($\text{Mg}_x\text{Ni}_{1-x}\text{O}$ and $\text{Mg}_y\text{Ni}_{1-y}\text{Al}_2\text{O}_4$, respectively). The Mg^{2+} content in the halite phase played important

roles in determining the activity of the lattice oxygen in the oxygen carriers, *i.e.* more Mg^{2+} in the halite phase corresponds to less reactive oxygen carriers during reduction. This effect was reduced over redox cycles owing to a net migration of Mg^{2+} from the halite phase to the spinel phase as a result of phase segregation. Furthermore, the unreactive solid solution can be regenerated by annealing the activated, cycled samples in N_2 at 800 °C over a period without redox reaction. This experimental investigation demonstrates the potential complexity of the solid state chemistry that must be appreciated during the formulation of synthetic oxygen carriers for high temperature chemical looping applications.

Chapter 5 Phase Interactions in Ni-Cu-Al₂O₃ Oxygen Carriers over Chemical Looping Methane Oxidation

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5.1 Introduction

CCS offers a mid-term solution to the decarbonization of the energy sector, as well as being part of the global effort to combat and mitigate anthropogenic climate change [3, 92, 93]. In CCS, the capture of CO₂ is responsible for the majority of the additional costs and energy penalty associated with this scheme. As an alternative to conventional carbon capture technologies, CLC enables the combustion of carbonaceous fuels under a nitrogen-free environment, removing the need for gas-phase separation in the first place [9, 11, 14, 94-98]. In essence, CLC is achieved by extracting and transporting oxygen from air to a combustor using redox-active metal oxides, termed oxygen carriers.

In CLC, the conversion of fuel to CO₂ is generally accompanied by side reactions, producing CO and solid carbon, especially when there is insufficient supply of oxygen to the gas phase, *e.g.* if the oxygen carriers are depleted of redox-active lattice oxygen (RALO) [99-101]. In general, carbon deposition is undesirable in CLC for two reasons. Firstly, the deposited carbon will be subsequently oxidized and released

as CO₂ when the oxygen carriers are regenerated in air, reducing the overall carbon capture efficiency. Secondly, the combustion of carbon in air will introduce temperature surges at the surface of oxygen carriers, shortening the life-span of the oxygen carriers by accelerating sintering [102, 103]. For the CLC of CH₄, there are two pathways of carbon formation: via (i) catalytic decomposition of CH₄ (Equation 5.1) and (ii) the Boudouard reaction (Equation 5.2). At high temperatures, *e.g.* above 800 °C, reaction (1) is the dominating cause of carbon deposition [104].

Over the past few years, some researchers found that in CLC of CH₄, for Cu- and Ni-based oxygen carriers, carbon deposition could be suppressed by raising the operating temperature above 800 °C [105-107], while others reported the opposite [103]. This disagreement may arise from the differences in the surface composition of the oxygen carrier that catalyzes the CH₄ decomposition. Nevertheless, there is a universal agreement on other driving forces for carbon deposition, *viz.* high pressure, high CH₄ concentration, and low availability of RALO [57, 99, 103, 108, 109].

Common process-level approaches to mitigate carbon deposition include: (i) adding steam to combustion at the expense of extra thermodynamic irreversibility [57, 107, 110, 111], and (ii) limiting the extent of oxygen carrier reduction at the expense of a much higher solid circulation rate in the circulating fluidized bed CLC system. Alternatively, carbon deposition can be controlled by designing and synthesizing oxygen carriers of specific compositions. For example, carbon formation can be

suppressed by supporting looping agents on redox-active materials, such as YSZ, ZrO_2 and CeO_2 [110, 112-116]. Doping oxygen carriers with alkaline metals (*e.g.* K^+) was also found to be effective against carbon formation [117-119]. Porous materials (*e.g.* zeolite) have been reported capable of providing physical barriers for coke deposition on oxygen carriers [120]. Furthermore, there have been reports of reduced carbon deposition when using mixtures of two or more looping agents, such as NiO-CoO , $\text{CuO-Fe}_2\text{O}_3$, and NiO-WO_3 as oxygen carriers [91, 121, 122].

In this work, we investigated a series of nickel-copper-aluminum mixed oxides as oxygen carriers for chemical looping conversion of CH_4 . NiO is well-known for its high activity in CH_4 conversion with high oxygen transfer capacity, but suffers from a major drawback - high activity towards carbon deposition. CuO is relatively resistant to carbon deposition, but less reactive towards CH_4 and highly prone to sintering at typical operating conditions of CLC. Accordingly, we hypothesize that mixed oxides of NiO-CuO would carry the advantages of both oxides, *e.g.* high activity towards CH_4 , resistance to carbon deposition and high oxygen transfer capacity.

5.2 Results and discussion

5.2.1 Characterization of the LDH precursors

The successful synthesis of the LDH precursors was confirmed by XRD (Figure 5.1(a)), which show the characteristic (003) and (006) diffraction peaks of LDHs at *ca.* 10° and 20° , respectively. All synthesized LDHs have platelet morphology with size increasing along with the content of Cu, as shown in Figure 5.1(b-f).

Figure 5.1 XRD patterns (a) and SEM images (b-f) of the as-prepared Ni/Cu/Al LDHs with varying Ni/Cu/Al ratios. The molar ratio of $(\text{Ni}^{2+} + \text{Cu}^{2+}) : \text{Al}^{3+}$ was fixed at 3:1, whereas the ratios of $\text{Ni}^{2+} : \text{Cu}^{2+}$ were (i) 3:0, (ii) 2.5:0.5, (iii) 2:1, (iv) 1:2 and (v) 0:3, corresponding to the samples from (b) to (f), respectively.

Figure 5.2 (a) Sample mass as a function of time during N_2 decomposition and H_2 reduction. (b) First-order derivative of mass as a function of time. The black dash lines show the temperature profiles over time.

5.2.2 Compositional analysis of the oxygen carriers by TGA

The elemental composition of the oxide samples was estimated based on thermal analysis. Figure 5.2(a) shows the normalized weight loss curves, from which the compositions are quantified as shown in Table 5.1. From Table 5.1, it is obvious that the ratios of divalent cations to trivalent cations in the mixed oxides are less than the intended ratio of 3:1. Thus, the oxygen carriers are named based on the calculated molar ratios of Ni:Cu:Al, *viz.* Ni_{1.32}Al, Ni_{0.94}Cu_{0.46}Al, Ni_{0.32}Cu_{0.90}Al, Ni_{0.12}Cu_{0.71}Al and Cu_{0.80}Al, which corresponds to samples 1 – 5 in Figure 5.1, respectively. Based on the cationic compositions, the theoretical maximum oxygen transfer capacities (OTC) are also calculated and displayed in Table 5.1.

Table 5.1 The composition of various metal oxide samples, calculated from thermogravimetric analysis involving Cu(II) decomposition and Cu(I) and Ni(II) reduction.

Oxygen carrier	Oxide basis (wt.%)			OTC mmol O/g	Nominal composition (mol.%)*			
	NiO	CuO	Al ₂ O ₃		NiAl ₂ O ₄	CuAl ₂ O ₄	NiO	CuO
Ni _{1.32} Al	65.8	0	34.2	8.84	38.0		62.0	
Ni _{0.94} Cu _{0.46} Al	44.4	23.3	32.3	8.87	35.7		31.3	33.0
Ni _{0.32} Cu _{0.90} Al	16.2	49.0	34.8	8.33	26.0	15.0		59.0
Ni _{0.12} Cu _{0.71} Al	7.8	48.3	43.9	7.12	14.7	45.7		39.6
Cu _{0.80} Al	0	55.3	44.7	6.95		62.7		37.3

*The calculation assumes (i) Al₂O₃ reacts preferentially with NiO to form NiAl₂O₄ and (ii) following (i), any residual Al₂O₃ reacts with CuO to form CuAl₂O₄.

The first derivatives of the mass loss curves during Cu(II) decomposition, as shown in Figure 5.2(b), consist of two peaks, which correspond to the decomposition of CuO and CuAl₂O₄ to Cu₂O and CuAlO₂, respectively [123]. From Figure 5.2(b), it can be seen that the second peak, which corresponds to the amount of CuAl₂O₄, reduces drastically with increase in Ni content. Among the five samples, Ni_{0.32}Cu_{0.90}Al has less amount of CuAl₂O₄ compared with the Cu²⁺-rich samples of Ni_{0.12}Cu_{0.71}Al and Cu_{0.80}Al, suggesting that Al₂O₃ preferentially reacts with NiO to form NiAl₂O₄.

Figure 5.3 SEM images of the fresh oxygen carriers, namely (a) Ni_{1.32}Al, (b) Ni_{0.94}Cu_{0.46}Al, (c) Ni_{0.32}Cu_{0.90}Al, (d) Ni_{0.12}Cu_{0.71}Al, and (e) Cu_{0.80}Al. (f) SXRD diffraction patterns of the fresh oxygen carriers, incident beam energy = 35 keV.

5.2.3 Characterization of fresh oxygen carriers

The Ni-Cu-Al mixed oxides show the platelet morphologies resembling those of the corresponding LDH precursors (Figure 5.3), with minor degrees of agglomeration and fracture due to sintering and thermal stress. Figure 5.3(f) shows the SXRD patterns of freshly synthesized mixed metal oxides, which are analyzed by Rietveld refinement with all reflection peaks fully indexed. The key refinement results, including phase identification, are shown in Table 5.2. From the SXRD results, three phases are identified, *viz.* a NiO phase (rock salt structure), a spinel phase and a CuO phase (tenorite structure). The spinel phase is a product of solid solution by NiAl_2O_4 and CuAl_2O_4 , *i.e.* $(\text{Ni,Cu})\text{Al}_2\text{O}_4$. Table 5.2 suggests absence of the NiO phase in $\text{Ni}_{0.32}\text{Cu}_{0.90}\text{Al}$ and $\text{Ni}_{0.12}\text{Cu}_{0.71}\text{Al}$, meaning that the majority of Ni^{2+} form spinel with Al_2O_3 . Table 5.2 also shows that the lattice parameter of NiO increases with the Cu^{2+} content, whereas that of CuO decreases with the Ni^{2+} content, suggesting that the NiO phase and the CuO phase are doped with Cu^{2+} and Ni^{2+} , respectively. In fact, CuO and NiO can form partial solid solution in one another [124]. However, the low mutual solubility (< 20 mol.% at 975°C , which decreases drastically with decreasing temperature) in the NiO-CuO system implies that the two phases can be largely referred as NiO and CuO for simplicity.

Figure 5.4 Normalized weight loss curves and their first-order time derivatives for temperature programmed reduction of the fresh oxygen carriers.

TPR in 5 vol.% H_2/N_2 was performed in TGA to investigate the types of RALO. Figure 5.4 shows the mass loss curves and their first derivatives. Amongst the samples, four types of RALO can be identified, *viz.* RALO in CuO (243~272 °C), CuAl_2O_4 (~432 °C), NiO (441~562 °C) and NiAl_2O_4 (>800 °C). It is generally expected that a TPR peak at low temperature corresponds to high RALO activity, and vice versa. Overall, the phases identified by TPR match well with the results of the compositional analyses as shown in Tables 5.1 and 5.2. Additionally, the TPR experiments further confirm the preferred formation of NiAl_2O_4 over CuAl_2O_4 .

We observe another interesting phenomenon that the reduction peak corresponding to CuO shifts to lower temperatures with higher Ni^{2+} content, meaning that doping CuO with Ni^{2+} can promote the activity of the RALO in CuO. The same promotion effect has also been found in reduction of NiO doped with Cu^{2+} (~335 °C), suggesting a synergetic effect. However, the TPR peaks corresponding to CuAl_2O_4 and NiAl_2O_4 shift to higher temperatures in the Ni-Cu- Al_2O_3 mixed samples, suggesting that the formation of the $\text{Ni}_x\text{Cu}_{1-x}\text{Al}_2\text{O}_4$ solid solution retards the activity of the RALO in respective spinel compounds. The same effect has been reported by Gayán et al., although the authors did not address the shift of the TPR peaks [125].

Table 5.2 Key parameters for the refinement of the SXRD patterns of the fresh oxygen carriers.

Sample	Phase	Lattice parameters			
		a (Å)	b (Å)	c (Å)	β (°)
1-Ni_{1.32}Al	NiO	8.3541	8.3541	8.3541	
	NiAl ₂ O ₄	8.0539	8.0539	8.0539	
2-Ni_{0.94}Cu_{0.46}Al	NiO	8.3766	8.3766	8.3766	
	NiAl ₂ O ₄	8.0567	8.0567	8.0567	
	CuO	4.6767	3.4339	5.1316	99.254
3-Ni_{0.32}Cu_{0.90}Al	CuO	4.6775	3.4330	5.1317	99.293
	(Ni,Cu)Al ₂ O ₄	8.0598	8.0598	8.0598	
4-Ni_{0.12}Cu_{0.71}Al	CuO	4.6867	3.4240	5.1321	99.438
	(Ni,Cu)Al ₂ O ₄	8.0721	8.0721	8.0721	
5-Cu_{0.80}Al	CuO	4.6888	3.4224	5.1324	99.44
	CuAl ₂ O ₄	8.0799	8.0799	8.0799	

5.2.4 Chemical looping oxidation of CH_4

5.2.4.1 Chemical looping cycles

It has to be emphasized that the experiment presented in this work is not designed to mimic any continuous chemical looping processes, but an investigation of the reaction between CH_4 and the oxygen carrier over a range of oxidation states. Figure 5.5 displays the product distribution from chemical looping CH_4 conversion over time in the 2nd and 100th cycle. The mole fraction of steam was not explicitly measured, but calculated from the hydrogen balance based on CH_4 and H_2 . Here, we identify three reaction stages: Stage I, manifested by a CO_2 peak and a H_2O peak with similar profile and twice the magnitude, corresponds to the complete combustion of CH_4 , producing CO_2 and H_2O . Stage II, manifested by a CO peak and a H_2 peak with similar profile and twice the magnitude, corresponds to the reforming of CH_4 to CO and H_2 . Stage III, manifested by the sole production of H_2 in the absence of CO , corresponds to the decomposition of CH_4 , producing H_2 and carbon. The three reaction stages took place consecutively with gradual transitions in-between. In particular, one can see in Figure 5.5(c) that the profile of CO_2 presents two peaks with the second peak stacking with the rising fraction of CO . The first peak is ascribed to the direct combustion of CH_4 , while the second peak is from the consecutive combustion of syngas, suggesting the enhanced oxygen carrier reactivity by CH_4 reforming [126].

Figure 5.5 Mole fraction of gaseous products during chemical looping CH_4 conversion with 5 vol.% CH_4/N_2 at 800 °C at the 2nd and 100th cycle. (a) $\text{Ni}_{1.32}\text{Al}$, (b) $\text{Ni}_{0.94}\text{Cu}_{0.46}\text{Al}$, (c) $\text{Ni}_{0.32}\text{Cu}_{0.90}\text{Al}$, (d) $\text{Ni}_{0.12}\text{Cu}_{0.71}\text{Al}$ and (e) $\text{Cu}_{0.80}\text{Al}$.

In a continuous process, chemical looping combustion can be facilitated by stopping the CH_4 feed before Stage I becomes kinetically unfavorable. The partially reduced oxygen carrier can then be transferred to a second reactor, where CH_4 reforming takes place via Stage II, producing syngas. The reforming reaction should be terminated before Stage III becomes kinetically significant. Figure 5.5 shows that

the product distribution profiles for $\text{Ni}_{0.94}\text{Cu}_{0.46}\text{Al}$, $\text{Ni}_{0.12}\text{Cu}_{0.71}\text{Al}$ and $\text{Cu}_{0.80}\text{Al}$ remain largely unchanged over 100 redox cycles, whereas the product distribution profiles for $\text{Ni}_{1.32}\text{Al}$ and $\text{Ni}_{0.32}\text{Cu}_{0.90}\text{Al}$ in the 100th cycle significantly differ from those in the 2nd cycle, suggesting structural or compositional changes during the reaction.

Figure 5.6 (a) CH_4 conversion, (b) normalized CO_2 yield, (c) CO yield and (d) carbon deposition on different $\text{NiO-CuO-Al}_2\text{O}_3$ oxygen carriers during 100 chemical looping redox cycles.

The performances of different oxygen carriers over 100 cycles of chemical looping are further compared using CH_4 conversion, yield of CO_2 , CO and carbon deposition as indicative parameters, as shown in Figure 5.6. Here, the yield of CO and CO_2 were calculated by integrating the gas concentration profiles during CH_4 conversion, whereas carbon deposition was quantified based on the amount of CO and CO_2

produced during the subsequent oxidation in 5 vol.% O₂. The results confirm a closed carbon cycle. Figure 5.6 shows that the performances of most oxygen carriers, except Ni_{1.32}Al and Ni_{0.32}Cu_{0.90}Al, are approximately consistent between the 10th and the 100th cycle. In general, higher Ni content leads to higher CH₄ conversion, lower CO₂ yield, higher CO yield and more carbon deposition. In particular, the amount of carbon deposition on Ni_{1.32}Al and Ni_{0.94}Cu_{0.46}Al is an order of magnitude higher than that on the other samples. Cu_{0.80}Al is most selective towards complete combustion of CH₄ with CO₂ yield close to 97% of the theoretical maximum (3.14 mmol g_{CuO}⁻¹). This observation is in accordance with the general knowledge that Cu-based oxygen carriers are selective towards complete combustion, whereas Ni-based oxygen carriers are highly active towards partial oxidation and CH₄ decomposition [98, 99].

In chemical looping, the reactivity of RALO is typically characterized by the change in solid conversion (according to Equation 3.17), in which zero stands for fully oxidized condition and unity corresponds to fully reduced condition. Here, the overall conversion over 100 redox cycles and the change in solid conversion over the 300 s reaction period in selected cycles are shown in Figure 5.7(a-e). Figure 5.7(f) shows that the conversion of all examined oxygen carriers are above 80% throughout the chemical looping experiments, which is a clear sign of high RALO reactivity. All samples except Ni_{0.32}Cu_{0.90}Al show stable rate of conversion profiles over cycling, suggesting absence of any bulk deactivation resulting from sintering. This could be a result of high sintering tolerance rendered by mixed oxides, the porous platelet structure, or a combination of both factors [56].

Figure 5.7 (a-e) The reduction curves of different $\text{NiO-CuO-Al}_2\text{O}_3$ oxygen carriers in selected cycles: 2nd, 10th, 20th, 50th and 100th. (f) Solid conversion during reduction with 5 vol.% CH_4/N_2 .

Some changes in behavior of oxygen carriers over chemical looping cycles are noticed. Firstly, the CH_4 conversion, CO_2 yield and carbon deposition on $\text{Ni}_{1.32}\text{Al}$ decrease over cycles, while the CO yield increases. In particular, the specific amount of carbon deposition on $\text{Ni}_{0.94}\text{Cu}_{0.46}\text{Al}$ surpasses that on $\text{Ni}_{1.32}\text{Al}$ after 40 cycles. This change in performance is probably a result of change in surface composition that influences the catalytic activity. Secondly, the CH_4 conversion, CO yield and carbon deposition on $\text{Ni}_{0.32}\text{Cu}_{0.90}\text{Al}$ increase over cycles. This activation of $\text{Ni}_{0.32}\text{Cu}_{0.90}\text{Al}$ towards partial oxidation of CH_4 to CO is correlated to the increased RALO activity as shown in Figure 5.7(c), which will be discussed later.

Figure 5.8 shows the complete set of selectivities towards carbon (S_c), CO_2 , CO and H_2 with the values at the 100th cycle summarized in Figure 5.9. It is obvious that

carbon deposition is severe on $\text{Ni}_{1.32}\text{Al}$ ($S_c = 16.1\%$) and $\text{Ni}_{0.94}\text{Cu}_{0.46}\text{Al}$ ($S_c = 29.6\%$), and significantly suppressed with increasing content of CuO. Interestingly, the carbon selectivity for $\text{Ni}_{0.32}\text{Cu}_{0.90}\text{Al}$ ($S_c = 6.7\%$) and $\text{Ni}_{0.12}\text{Cu}_{0.71}\text{Al}$ ($S_c = 3.9\%$) is less than that for $\text{Cu}_{0.80}\text{Al}$ ($S_c = 9.0\%$), despite Ni being catalytically active for CH_4 decomposition. In addition, the mitigation of carbon deposition on $\text{Ni}_{0.32}\text{Cu}_{0.90}\text{Al}$ and $\text{Ni}_{0.12}\text{Cu}_{0.71}\text{Al}$ is achieved at the expense of reduced CO_2 selectivity, and the underlying origin will be discussed later.

Figure 5.8 Selectivity of CO_2 , CO, carbon and H_2 during oxygen carrier reduction with 5 vol.% CH_4 in 100 chemical looping cycles.

Figure 5.9 CH₄ conversion and selectivity of H₂, carbon, CO and CO₂ in the 100th reduction cycle for different NiO-CuO-Al₂O₃ oxygen carriers with 5 vol.% CH₄/N₂.

By comparing the performance of the oxygen carriers (Figure 5.6) with their compositions (Table 5.1 and Figure 5.4), it is apparent that significant carbon deposition occurs only when the samples contain free NiO, which can be reduced to metallic Ni and catalyze carbon deposition, *i.e.* in the case of Ni_{1.32}Al and Ni_{0.94}Cu_{0.46}Al. If Ni²⁺ is present only in the form of NiAl₂O₄, *i.e.* in the case of Ni_{0.32}Cu_{0.90}Al and Ni_{0.12}Cu_{0.71}Al, it cannot be so easily reduced to metallic Ni, while at the same time its RALO remains sufficiently reactive, providing an oxidizing environment that further inhibits the CH₄ decomposition. In Cu_{0.80}Al, CuO and CuAl₂O₄ are quickly reduced to a mixture of metallic Cu and Al₂O₃; neither is capable of providing RALO, which is a key to mitigate carbon deposition. On the other hand, the relatively unreactive RALO in (Ni,Cu)Al₂O₄ is only capable to partially oxidize CH₄ or the deposited carbon, resulting in the low CO₂ selectivity as observed for Ni_{0.32}Cu_{0.90}Al and Ni_{0.12}Cu_{0.71}Al.

Figure 5.10 SXRD patterns of the spent Ni-Cu-Al₂O₃ oxygen carriers.

5.2.4.2 Change in phase and composition of oxygen carriers during chemical looping

We further measured the SXRD patterns of the oxygen carriers after chemical looping cycles (Figure 5.10), which show that the phase and composition of samples Ni_{0.94}Cu_{0.46}Al, Ni_{0.12}Cu_{0.71}Al and Cu_{0.80}Al remain relatively unchanged as compared with the fresh ones, in agreement with their stable performances as shown in Figure 5.6. The composition of Ni_{1.32}Al and Ni_{0.32}Cu_{0.90}Al changed significantly over the looping cycles, which account for their dramatic changes in performance as described in section 5.2.4.1.

For Ni_{1.32}Al and Ni_{0.32}Cu_{0.90}Al, the changes in SXRD diffraction patterns and TPR profiles are plotted in Figure 5.11. Figure 5.11(a) shows that after 100 redox cycles, the diffraction peaks of NiO and NiAl₂O₄ shift to lower and higher diffraction angles, respectively. This can only be explained by a net migration of the dissolved Al₂O₃ from the NiO phase to the NiAl₂O₄ phase, in which more dissolved Al₂O₃ gives

smaller lattice parameters [127]. In addition, the dissolved Al_2O_3 would further hinder the reactivity of RALO in the mother phase. Therefore, the TPR peaks for NiO and NiAl_2O_4 shift to lower and higher temperatures, respectively, as shown in Figure 5.11(b). The enrichment of Al_2O_3 in NiAl_2O_4 shall also be responsible for the decrease in CO_2 yield and the increase in CO yield, as shown in Figure 5.6(b-c). It should be noted that, in Figure 5.11(b), the low temperature ($< 450^\circ\text{C}$) and high temperature ($> 530^\circ\text{C}$) peaks associated with NiO reduction can be assigned to two types of NiO which have weak (α -type) and middle (β -type) interaction with the Al_2O_3 support compared with the strong interaction in NiAl_2O_4 spinel, respectively [128]. Accordingly, the enhancement of α -type peak and the reduction of β -type peak suggest an overall segregation of NiO from Al_2O_3 support.

Figure 5.11 SXR patterns (a & c) and TPR curves (b & d) of the fresh and spent $\text{Ni}_{1.32}\text{Al}$ and $\text{Ni}_{0.32}\text{Cu}_{0.90}\text{Al}$.

The NiO diffraction peaks as shown in Figure 5.11(c) indicate the precipitation of the NiO phase from the original NiO-free $\text{Ni}_{0.32}\text{Cu}_{0.90}\text{Al}$ after cycling. It should also be noted that the sharp Al_2O_3 peak in Figure 5.11(c) comes from the contamination of the packing material used for the chemical looping experiments. In the TPR profile as shown in Figure 5.11(d), the shift of the CuO peak from 261 to 275 °C, corresponding to loss of Ni^{2+} in the CuO phase, also suggests the precipitation of NiO, which is probably caused by the cumulative phase segregation over fast redox cycles at low temperature, a phenomenon discussed in detail by Huang *et al* [129]. The precipitated NiO, albeit little, is responsible for the increase in RALO reactivity, CH_4 conversion and CO yield on $\text{Ni}_{0.32}\text{Cu}_{0.90}\text{Al}$. However, the presence of free NiO, which is easily reducible to Ni, also means more carbon deposition on $\text{Ni}_{0.32}\text{Cu}_{0.90}\text{Al}$ in the chemical looping cycles.

5.3 Summary

In summary, we prepared a series of nickel-copper-aluminum mixed oxides with varying Ni:Cu ratios from Ni/Cu/Al LDH precursors and investigated their performance as oxygen carriers for chemical looping conversion of CH_4 . The platelet structure of mixed oxides inherited from their parent LDHs renders stable lattice oxygen reactivity to all oxygen carriers over 100 redox cycles at 800 °C. In the NiO-CuO- Al_2O_3 system, formation of NiAl_2O_4 spinel is favoured over CuAl_2O_4 and the oxygen activity in the spinel phase decreased by forming stable $(\text{Ni,Cu})\text{Al}_2\text{O}_4$ solid solution. Doping Ni^{2+} to CuO and Cu^{2+} to NiO could promote the reactivity of

RALO in both phases. However, the presence of any NiO phase would inevitably lead to severe carbon deposition. Furthermore, (Ni,Cu)Al₂O₄ was found to be an excellent retardant to carbon deposition, despite its low selectivity towards complete combustion of CH₄. An ideal design of a NiO-CuO-Al₂O₃ oxygen carrier for chemical looping CH₄ conversion needs to include a Ni²⁺ doped CuO phase supported on (Ni,Cu)Al₂O₄ spinel. Such an oxygen carrier is best utilized over redox cycles that comprise of a combustion stage, a reforming stage and a regeneration stage.

Chapter 6 High-Performance Ni-Fe Redox Catalysts for Selective

CH₄ to Syngas Conversion via Chemical Looping

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6.1 Introduction

Syngas is an important raw material for production of a variety of value-added chemicals such as ethanol and gasoline through methanol or Fischer-Tropsch synthesis [130-133]. Biomass, natural gas and coal can be used to make syngas through steam or CO₂ reforming, partial oxidation, and gasification [134]. In industry, steam reforming of natural gas has been successfully executed to produce molecular H₂. However, this strong endothermic reforming process is unfortunately restricted by thermodynamics and energy intensive, which requires complicated purification processes [135]. Alternatively, chemical looping steam reforming of methane (CLSRM) provides a promising technology to make both syngas and pure H₂ in two separated steps simultaneously without undergoing any tedious purification processes [91, 136-143]. But, the CH₄ conversion is greatly limited in CLSRM by the amount of the available lattice oxygen in the oxygen carrier, and at the same time, carbon deposition poses severe issues to contaminate the produced H₂, as well as to cause catalyst deactivation [102, 103].

To make CLSRM an industrially viable process, herein, we propose to include steam gasification in CLSRM. With this new process, we expect to achieve: (i) higher CH_4 conversion, which is thermodynamically favored, (ii) higher selectivity to CO through selective gasification of deposited carbon to syngas, (iii) minimal water gas shift reaction, which shall favor high CO selectivity, (iv) less degree of catalyst sintering, and (v) possible heat integration between the stepwise reactions. To realize all these benefits, the catalyst development becomes critical, in which high reactivity for CH_4 oxidation, steam regeneration and high catalytic activity for CH_4 decomposition are required.

Iron has been proven active in water splitting for H_2 production since 1903 [63], while Ni-based catalysts are widely used in traditional steam reforming of natural gas. By combining the advantages of the Ni and Fe species, thus we anticipate that the Ni-Fe binary catalyst shall be active for the CLSRM coupled with CH_4 decomposition. In this work, we designed a series of Ni-Fe redox catalysts with varying Ni/Fe ratios. The optimized Ni-Fe catalyst with equimolar of Ni and Fe could achieve CH_4 conversion of 97.5% and CO selectivity of 92.9% at 900 °C with excellent cycling stability.

6.2 Results and discussion

6.2.1 Characterization of the fresh Ni-Fe redox catalysts

Layered double hydroxides (LDH) are a class of 2-dimensional lamellar material consisted of positively charged brucite-like layers with anions and solvation

molecules in the interlayer for the charge neutralization. The Ni-Fe redox catalysts were synthesized by calcining the co-precipitated LDH precursors, to maximize the dispersion of Ni and Fe atoms in the solid. The XRD patterns of the precipitates were shown in Figure 6.1. It can be found that the precipitated precursors with molar ratios of $\text{Ni}^{2+}:\text{Fe}^{2+}$ of 2:0, 1.5:0.5 and 1:1 (Figure 6.1(a-c)) showed the characteristic peaks of LDH at ~ 11.6 , 23.5 and 35.1° , while with higher Fe content the peaks can be indexed to goethite $\text{FeO}(\text{OH})$ (JCPDS 29-0713). In the preparation of Fe-containing samples, the colour of the slurry changed from pale green to orange during the aging at 60°C , suggesting that the Fe^{2+} was oxidized to Fe^{3+} by the oxygen in the air. The peak intensity decreased with increasing Fe content from sample 1# to 3#, indicating that Fe^{2+} oxidation contributed to the disorganisation of the LDH structure.

Figure 6.1 XRD patterns of the co-precipitated precursors for the Ni-Fe redox catalysts. The molar ratio of $(\text{Ni}^{2+}+\text{Fe}^{2+}):\text{Al}^{3+}$ was fixed at 2:1, and the ratios of $\text{Ni}^{2+}:\text{Fe}^{2+}$ were a) 2:0, b) 1.5:0.5, c) 1:1, d) 0.5:1.5, and e) 0:2, respectively. (f) shows the standard of $\text{FeO}(\text{OH})$ Goethite (JCPDS 29-0713).

The precipitated precursors were calcined at 1000 °C for 6 h to obtain the Ni-Fe redox catalysts with the equilibrium phase composition. Figure 6.2 displays the XRD patterns of the fresh full oxidized samples. For Ni₂Al, halite NiO and spinel NiAl₂O₄ phases were both detected, while the peaks of in Fe₂Al matched with Fe₂O₃ (JCPDS 33-0664). The absence of spinel FeAl₂O₄ in Fe₂Al can be ascribed to the inferior stability of divalent Fe²⁺ under air due to its irreversible oxidation to trivalent Fe₂O₃ during the calcinations. For all the Ni-containing samples, spinel phase (labeled with ♠ in Figure 6.2) was detected, with additional NiO (labeled with ♥) for Ni₂Al and Ni_{1.5}Fe_{0.5}Al with high Ni/Al ratio, or extra Fe₂O₃ (labeled with ♦) for Ni_{0.5}Fe_{1.5}Al with high Fe/Al ratio. It is noteworthy that only spinel was detected in NiFeAl, with peak positions in the between of NiFe₂O₄ and NiAl₂O₄ standards, indicating the formation of NiFe₂O₄ - NiAl₂O₄ solid solution.

Figure 6.2 XRD patterns of the fresh $\text{Ni}_x\text{Fe}_{2-x}\text{Al}$ redox catalysts: (a) Ni_2Al , (b) $\text{Ni}_{1.5}\text{Fe}_{0.5}\text{Al}$, (c) NiFeAl , (d) $\text{Ni}_{0.5}\text{Fe}_{1.5}\text{Al}$ and (e) Fe_2Al . The sloping grey dash lines show the spinel phase (♠), while NiO and Fe_2O_3 phases were labeled with ♥ and ♦, respectively. (f-j) are the standards of NiAl_2O_4 (JCPDS 10-0339), FeAl_2O_4 (JCPDS 34-01929), NiFe_2O_4 (JCPDS 54-0964), NiO (JCPDS 47-1049) and Fe_2O_3 (JCPDS 33-0664).

Figure 6.3 Solid conversions of fresh Ni-Fe redox catalysts during TPR (a) and TPO (b) with CO_2 . First-order derivatives of sample mass during TPR (c) and TPO (d).

The fresh catalysts were studied with TPR and TPO using TGA to verify the oxygen availability and the oxidizing property of the reduced catalysts during the following oxidation. Figure 6.3 shows the solid conversion and the first-order derivative of mass during TPR and TPO. It can be found in Figure 6.3(b) that the reduced Ni_2Al , $\text{Ni}_{1.5}\text{Fe}_{0.5}\text{Al}$ and NiFeAl could be full regenerated with CO_2 up to 1100 °C, while $\text{Ni}_{0.5}\text{Fe}_{1.5}\text{Al}$ and Fe_2Al achieved ~89% solid conversion. Theoretically, the phase change from metallic Fe to Fe_3O_4 contributes ~88.9% conversion of Fe- Fe_2O_3 couple. Therefore, the incomplete regeneration of the $\text{Ni}_{0.5}\text{Fe}_{1.5}\text{Al}$ and Fe_2Al can be ascribed to the oxidation of the reduced catalysts to Fe_3O_4 , and first mass loss of Fe_2Al TPR in the temperature range of ~320-380 °C can be assigned to the reduction

of Fe_2O_3 to Fe_3O_4 . In the case of Ni_2Al , the peaks shown in Figure 6.3(c) at ~ 526 and 829°C correspond to the reduction of halite NiO and spinel NiAl_2O_4 phases, respectively. For $\text{Ni}_{1.5}\text{Fe}_{0.5}\text{Al}$, two strong peaks in the TPR curve presented. The peak at $\sim 847^\circ\text{C}$ was due to the reduction of spinel phase, and the peak at $\sim 398^\circ\text{C}$ resulted from the reduction of Fe-modified NiO . This reduction temperature was $\sim 130^\circ\text{C}$ lower than that of pure NiO shown in the curve of Ni_2Al , suggesting the positive effects of Fe modification on the activity of NiO . For NiFeAl , only one strong and broad peak was found, which is in good agreement with its XRD pattern with the particular spinel phase presented. For $\text{Ni}_{0.5}\text{Fe}_{1.5}\text{Al}$ and Fe_2Al , each sample presented with 3 peaks, the complexity of the profiles originated from the multi-valent property of Fe species. As shown in Figure 6.3(d), the oxidation of reduced Ni_2Al and Fe_2Al during TPO presented single oxidation peak at ~ 950 and 490°C , respectively. For the binary catalysts, there are two peaks with partial overlapping, suggesting a stepwise oxidation of Fe and Ni.

6.2.2 Performance of the Ni-Fe redox catalysts for CH_4 to syngas conversion

To enhance syngas selectivity in CLSRM, the ratio of the reactive O in oxygen carrier catalyst to CH_4 should be kept low, which however unfavorably decreases the conversion of CH_4 and the productivity of syngas. Core-shell $\text{Fe}_2\text{O}_3@\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ perovskite was reported to be able to maintain high syngas selectivity in partial oxidation of CH_4 with relatively large ratios of oxygen to CH_4 by controlling the lattice oxygen transport between iron oxide particles and the shell surface [144].

However, such catalysts with well defined structure need further improvement to scale up the material syntheses for industrial interests. Therefore, it remains a great challenge to simultaneously realize both high CH₄ conversion and syngas selectivity in CLSRM. On the other hand, deep reduction of the oxygen carrier catalysts is generally desired to make full use of their oxygen transfer capacity in the chemical looping processes, while under such condition in CLSRM, carbon deposition is inevitable especially on Ni-based oxygen carriers. Instead of eliminating carbon deposition with assistance of other oxidants (steam or CO₂) [99, 107, 110, 111], we propose to chemically decompose CH₄ during the fuel conversion process. With the binary Ni-Fe redox catalysts developed in this work, the deposited carbon in CH₄ reduction could be gasified with steam to selectively produce syngas in a chemical looping scheme (Figure 3.2).

As shown in Figure 6.4(a), both CO selectivity of ~80% and CH₄ conversion above 95% were achieved using NiFeAl and Ni_{1.5}Fe_{0.5}Al redox catalysts in CLSRM cycles with O₂ regeneration at 900 °C. The CO selectivity could be further improved to 92.9% for the NiFeAl catalyst in the absence of O₂ regeneration, with a slightly decreased CH₄ conversion of 87.1%. The Ni-rich catalysts (Ni_{1.5}Fe_{0.5}Al and Ni₂Al) are very active in co-feeding steam reforming of CH₄ with ~97% CH₄ conversion. However, the selectivity to CO is only ~60%, which is significantly lower than that obtained from the looping reforming. The high CO selectivity of CLSRM is originated from the fact that the water gas shift reaction can be intrinsically hindered in a chemical looping scheme. Figure 6.4(b) compares the productivity of syngas and the H₂/CO

ratios. Among the best catalysts at various conditions, NiFeAl produces the largest amount of syngas per cycle in the absence of O₂ regeneration with a H₂/CO ratio of ~3. With O₂ regeneration, the syngas productivity slightly decreases, and the H₂/CO ratio for NiFeAl and Ni_{1.5}Fe_{0.5}Al are 3.24 and 2.84, respectively, while that for Ni_{1.5}Fe_{0.5}Al is ~4 from co-feeding reforming as a result of water gas shift reaction. Table 6.1 compares the performance of our binary Ni-Fe redox catalysts in CLSRM with those reported in the literature.

Figure 6.4 Performance of the typical Ni-Fe redox catalysts in CLSRM. (a) CH₄ conversion and CO selectivity, and (b) productivity of syngas and the H₂/CO ratio in steam reforming of CH₄ cycles for Ni-Fe redox catalysts.

Table 6.1 Performance comparison of different oxygen carriers (redox catalysts) for CH₄ to syngas conversion.

Ref.	Catalysts	CH ₄ conv. (%)	CO sele. (%)	Productivity (mol kg ⁻¹)		Experimental conditions
				CO	H ₂	
This work	NiFeAl	97.5	81.6	8.7	28.2	0.1 g catalyst, 900 °C, stage I: 5% CH ₄ /N ₂ , 5 min; stage II: 10 µL/min water carried by N ₂ , 5 min; stage III: 5% O ₂ /N ₂ , 5 min; gas flow rate: 110 mL/min
	Ni _{1.5} Fe _{0.5} Al	94.7	82.6	8.63	24.5	
	NiFeAl	87.1	92.9	9.6	29.0	Without stage III
	Ni _{1.5} Fe _{0.5} Al	97.2	59.4	6.57	26.7	Co-feeding of CH ₄ and steam
[137] ^a	CeO ₂	35	90	1.43	3.7 (re) 1.41 (ox)	1.8 g, 850 °C, reduction: 10 mL/min CH ₄ (20 min); oxidation: 0.18 cm ³ /min H ₂ O carried by N ₂ (50 mL/min, 30 min)
	Ce _{0.5} Fe _{0.5} O _{2-δ}	77	86	3.58	7.23 (re) 4.93 (ox)	900 °C
[145] ^b	Ce–ZrO ₂ (Ce:Zr = 7:3)	~50	78	0.68	1.36 (re) 1.59 (ox)	Similar with [137], 850 °C, reduction time: 5 min
[115]	10%CeO ₂ /LaFeO ₃	~54	90	3.31	6.63 (re) 3.38 (ox)	0.3 g, 800 °C, 5% CH ₄ /Ar, 5 min; steam was generated by heating water at 60 °C and N ₂ was bubbled to carry the steam; gas flow rate: 200 mL/min
[146] ^c	Ni(8.8)/CeO ₂	95	96	0.93 (re) 1.01(CO ₂ splitting)	1.86 (re)	0.2 g, 800 °C, reduction: 5% CH ₄ , 1 min; oxidation: 5% CO ₂ , 1 min; gas flow rate: 100 mL/min
[142] ^d	BaMn _{0.5} Fe _{0.5} O ₃	95	88			20 g, 900 °C, reduction: 3.2 mL/min CH ₄ ; oxidation: 2.34 mol% steam, both carried by 200 mL/min N ₂
[143]	La _{1.6} Sr _{0.4} FeCoO ₆	90	40		5.9 (ox)	2.0 g, 850 °C, reduction: 40% CH ₄ /N ₂ ; oxidation: 0.2 mL/min water carried by N ₂ , 20 min; gas flow rate: 50 mL/min
[147] ^e	Macroporous LaFeO ₃	~50	~60	0.58	1.51 (re) 1.53 (ox)	1.0 g, 850 °C, reduction: 40% CH ₄ /N ₂ , 10 min; oxidation: 0.18 mL/min water carried by N ₂ , 20 min; air oxidation; gas flow rate: 50 mL/min
[148]	LaSrFeCoO ₆	78	87		4.0 (ox)	2.0 g, 850 °C, reduction: 40% CH ₄ /N ₂ , 12 min; oxidation, 0.2 mL/min water carried by N ₂ , 15 min.; air, 10 min; gas flow rate: 50 mL/min
[149]	Sr ₃ Fe ₂ O _{7-δ} –CaO nanocomposites	59	90	1.48 (re) 2.17(CO ₂ splitting)	3.15 (re)	980 °C, WHSV: 12000 cm ³ g _{Sr₃-C} ⁻¹ h ⁻¹ ;

^aThe production of H₂ and CO (mL) on Ce_{0.5}Fe_{0.5}O_{2-δ} was extracted from Figure 8.

^bThe production of H₂, CO and CO₂ (mL) was extracted from Figure 3, and the data in the 10th cycle was used.

^cThe production of H₂ and CO (mL) was calculated based on the CH₄ and CO₂ conversion, CO selectivity and the amount of introduced CH₄ (5 mL) and CO₂ (5 mL). Only short cycle time was applicable to achieve high CH₄ conversion and CO selectivity, and the frequent gas switch shall restrict the overall efficiency.

^dHigh CH₄ conversion of 95% was obtained with large oxygen carrier to CH₄ ratio.

^eThe production of H₂, CO and CO₂ (mL) was extracted from Figure 7, and the data in the 10th cycle was used.

6.2.3 Effect of Ni/Fe ratio

To understand the outstanding performance, the Ni-Fe redox catalysts with varying compositions were investigated in CLSRM at different temperatures, as well as in co-feeding reforming and CLSRM without O₂ regeneration. The typical gas molar fraction profiles in the 30th cycle of CLSRM are depicted in Figure 6.5. In stage I, it can be observed that both single Ni- and Fe-based catalysts (Ni₂Al, Fe₂Al) display higher CH₄ percentage at the exit of the reactive bed as compared to the binary Ni-Fe catalysts (Ni_{1.5}Fe_{0.5}Al, NiFeAl and Ni_{0.5}Fe_{1.5}Al), suggesting enhanced reactivity for CH₄ conversion on the binary catalysts. In stage II, it is found that the Ni-containing catalysts produced CO and H₂ with a small portion of CO₂, while pure H₂ was generated during oxidation of reduced Fe₂Al with steam.

Figure 6.5 The profiles of gas volumetric fraction in the 30th cycle of CLSRM at 900 °C on various Ni-Fe redox catalysts. (a) Ni₂Al, (b) Ni_{1.5}Fe_{0.5}Al, (c) NiFeAl, (d) Ni_{0.5}Fe_{1.5}Al and (e) Fe₂Al. The three reaction stages including CH₄ reduction (stage I: 5 vol.% CH₄/N₂ 110 mL/min), steam gasification (stage II: N₂ 110 mL/min, water 10 μL/min) and O₂ regeneration (stage III: 5 vol.% O₂/N₂ 110 mL/min) are separated by dash lines.

Figure 6.6 Effect of Ni/Fe composition on the performance of the catalysts. (a) CH_4 conversion of various Ni-Fe redox catalysts during 5 vol.% CH_4/N_2 reduction. (b) Productivity of H_2 , CO and CO_2 in 5 vol.% CH_4/N_2 reduction (stage I) and steam oxidation (stage II). The data presented in (a) and (b) are the average values of cycles 26-30.

Figure 6.7 CH₄ conversion during stage I on various Ni-Fe redox catalysts. Condition: 0.1 g of catalyst, 5 vol.% CH₄/N₂ at a flow rate of 110 mL/min for 5 min at 900 °C.

Figure 6.8 The selectivity of H₂, CO, CO₂ and carbon deposition during stage I for various Ni-Fe redox catalysts. (a) Ni₂Al, (b) Ni_{1.5}Fe_{0.5}Al, (c) NiFeAl, (d) Ni_{0.5}Fe_{1.5}Al and (e) Fe₂Al. (f) shows the CO/(CO+CO₂) ratio as a function of cycle number.

Table 6.2 Average value for CH₄ conversion and selectivity to CO₂, CO, C and H₂ in stage I of cycles 26-30.

Catalyst	CH ₄ conversion / %	Selectivity / %			
		CO ₂	CO	C	H ₂
Ni ₂ Al	43	40.8	33	26.2	54
Ni _{1.5} Fe _{0.5} Al	93.5	14	27.2	58.8	74.8
NiFeAl	97.7	8.5	27.6	63.9	83.9
Ni _{0.5} Fe _{1.5} Al	81.7	11.7	28.6	59.6	74.8
Fe ₂ Al	21.6	44.7	53.4	1.9	54.2

Figure 6.6(a) compares the CH₄ conversion and CO selectivity in the CLSRM cycles for the Ni-Fe catalysts with different Ni/Fe ratios. Binary Ni-Fe catalysts show both superior CH₄ conversion and CO selectivity than the single Ni or Fe counterpart. The detailed CH₄ conversion is shown in Figure 6.7. For Ni₂Al, the CH₄ conversion was maintained stable at ~42% in 30 cycles. It took only 5 cycles for NiFeAl to achieve 95% CH₄ conversion, while it required ~15 and 25 cycles for Ni_{1.5}Fe_{0.5}Al and Ni_{0.5}Fe_{1.5}Al to stabilize and achieve CH₄ conversion exceeding 90% and 80%, respectively, suggesting excellent reactivity and stability of NiFeAl. Fe₂Al shows a continuous decrease of CH₄ conversion from ~50% to ~20%, indicating its poor stability. Among the five catalysts examined, the binary Ni-Fe catalysts exhibit not only enhanced CH₄ conversion, but also limited selectivity to CO₂. Figure 6.8 and Table 6.2 give the detailed selectivity to H₂, CO, CO₂ and C for various Ni-Fe catalysts in stage I. It can be seen from Figure 6.8(f) that all binary Ni-Fe catalysts possess higher values of CO/(CO+CO₂) as compared with single Ni or Fe counterpart. From Table 6.2, it is apparent that carbon deposition on reduced binary Ni-Fe

catalysts is much higher than that on Ni₂Al and Fe₂Al, with C selectivity following: NiFeAl (63.9%) > Ni_{1.5}Fe_{0.5}Al (59.6%) > Ni_{0.5}Fe_{1.5}Al (58.8%) > Ni₂Al (26.2%) > Fe₂Al (1.9%). In stage II, water was introduced into the hot bed with a flow rate of 10 µL/min carried by N₂ stream at 110 mL/min, which generated a stream of hot steam with volume concentration of ~11%. The deposited carbon in stage I could thus be gasified with steam to selectively produce CO and H₂, which further improves the CO selectivity in the overall cycle. The possible reactions occurring in stage II are listed as below:

Figure 6.6(b) shows the gas productivity on various Ni-Fe redox catalysts in stage I and II (detailed gas productivity in 30 cycles is shown in Figures 6.9 and 6.10). Apparently, the binary Ni-Fe catalysts exhibit significantly larger syngas productivity than the single Ni or Fe counterpart, among which, NiFeAl gives the largest CO productivity of 3.04 mol kg⁻¹ and 6.07 mol kg⁻¹ during the reduction and steam oxidation stages, respectively, indicating that CH₄ decomposition contributes ~67% of the CH₄ conversion. During reduction, the H₂/CO ratio on Fe₂Al was kept stable at ~2.0 (Figures 6.9(e) and 6.11), which is identical to the theoretical value for partial oxidation of CH₄. For Ni-containing redox catalysts, H₂ could be produced via both partial oxidation and decomposition of CH₄, resulting in larger H₂/CO ratios (> 2). The largest H₂/CO ratio was observed on NiFeAl, which also indicates the most

serious carbon deposition. The high CH_4 conversion and extensive carbon deposition on the binary Ni-Fe catalysts produced a concentrated H_2 stream during the reduction stage, with H_2 molar fraction as high as ~80% (Figure 6.12). During steam oxidation, both CO and H_2 productivity on binary Ni-Fe redox catalysts were remarkably comparable with those on Ni_2Al and Fe_2Al (Figure 6.6(b)), resulting from the gasification of solid carbon deposits (Equation 6.1) in stage I. The gasification of solid carbon generates syngas together with a small fraction of CO_2 (Figure 6.13) through the water gas shift reaction (Equation 6.2). Among various binary Ni-Fe catalysts, $\text{Ni}_{1.5}\text{Fe}_{0.5}\text{Al}$ shows the highest CO selectivity of 95% in the gasification (Figure 6.11(d)). The H_2/CO ratio in the gas mixture obtained after steam oxidation is in the range of 1.5 to 2.3 (Figure 6.11), which increases with increasing Fe content as a result of H_2 production from the iron steam process (Equation 6.3).

Figure 6.9 The gas productivity and carbon deposition during reduction of the Ni-Fe redox catalysts with 5 vol.% CH_4/N_2 . (a) CO_2 , (b) CO , (c) H_2 , (d) carbon deposition, and (e) H_2/CO ratio.

Figure 6.10 The syngas productivity during oxidation of reduced Ni-Fe redox catalysts with steam. (a) CO, (b) H₂, (c) H₂/CO ratio and (d) CO/(CO+CO₂) ratio.

Figure 6.11 H₂/CO ratio during CH₄ reduction, steam oxidation and the complete cycle on various Ni-Fe redox catalysts. The data presented are the average values from cycles 26-30.

Figure 6.12 Gas molar fraction of H_2 , CO , CO_2 and CH_4 during reduction of the Ni-Fe redox catalysts with 5 vol.% CH_4/N_2 (stage I).

Figure 6.13 Gas molar fraction of H_2 , CO , and CO_2 during oxidation of the reduced Ni-Fe redox catalysts with steam (stage II).

6.2.4 Effect of temperature

CLSRM cycles were performed at different temperatures from 700 to 900 °C with an interval of 50 °C to study the effect of reaction temperature. From Figure 6.14(a) and Figure 6.15, it can be seen that Ni₂Al gives similar CH₄ and steam conversion of ~40% and ~7% in the studied temperature range, while Fe₂Al exhibits bad reactivity with very low CH₄ and steam conversion. With 25% Fe substitution by Ni, Ni_{0.5}Fe_{1.5}Al displays significantly enhanced CH₄ and steam conversion at high temperatures, even better than that for Ni₂Al (at 850 and 900 °C). With further increase in the Ni content, both CH₄ and steam conversion can be improved simultaneously. For CO selectivity (Figure 6.14(b)), it keeps stable at ~58% for Ni₂Al in the studied temperature range, while Fe₂Al shows low selectivity to CO. The binary catalysts consisting of both Ni and Fe greatly increase the CO selectivity, reaching around 82% for NiFeAl at 900 °C. Figure 6.14(c) and (d) summarize the effects of both reaction temperature and catalyst composition on the CH₄ conversion and CO selectivity, demonstrating the optimized performance in the temperature range from 800 to 900 °C with Ni_{1.5}Fe_{0.5}Al or NiFeAl catalyst.

Figure 6.14 Effect of temperature on the performance. (a) CH₄ conversion and (b) CO selectivity for various Ni-Fe catalysts in the temperature range from 700 to 900 °C. (c) & (d) describe the effects of both temperature and composition on (c) CH₄ conversion and (d) CO selectivity.

Regarding to the gas productivity (Figure 6.16), the productivity of CO on Ni₂Al slightly increases with increasing temperature during reduction, but decreases during steam oxidation. The decrease of CO productivity in steam oxidation with temperature increasing can be explained by reduced carbon deposition at higher temperatures as shown in Figure 6.16(c), which agrees well with the reported carbon deposition behavior of the Ni-based oxygen carriers in chemical looping combustion [102, 106]. Carbon deposition on binary Ni-Fe catalysts increases with increasing

temperature during reduction, which leads to CO generation in the subsequent steam oxidation (stage II). Among the Ni-Fe binary catalysts, NiFeAl produces the largest amount of CO in the whole looping cycle (except at 800 and 850 °C). Besides, NiFeAl is also the best catalyst for H₂, which is most active for CH₄ decomposition at various testing temperatures. As shown in Figure 6.16(d), the H₂/CO ratio is determined by both the reaction temperature and the Fe content in the catalyst. With increasing temperature, there exists a general trend that the H₂/CO ratio decreases for each individual catalyst, opposite to the CO selectivity. At a fixed temperature, the H₂/CO ratio increases with the Fe content, as a result of additional H₂ produced from oxidation of reduced Fe species with steam.

Figure 6.15 Steam conversion in stage II on various Ni-Fe redox catalysts at temperature range from 700 to 900 °C.

Figure 6.16 Temperature effects on gas productivity on various Ni-Fe redox catalysts.

(a) CO and (b) H₂ during reduction and steam oxidation, (c) carbon deposition during reduction and (d) H₂/CO ratio in complete cycle.

Figure 6.17 Comparison of the performance on Ni-Fe redox catalysts in CLSRM

(with and without O₂ regeneration) and co-feeding reforming. (a) CH₄ conversion, (b)

CO selectivity for various Ni-Fe redox catalysts.

6.2.5 Effect of catalyst regeneration with O₂

To fully recover the oxidation states of the Ni-Fe redox catalysts, regeneration with O₂ after steam oxidation is required. CLSRM cycles with and without O₂ regeneration were thus performed at 900 °C to investigate the effect of O₂ regeneration on the performance of catalysts. As shown in Figure 6.17(a), it can be observed that CH₄ conversion is apparently lower for CLSRM without O₂ regeneration than the one with O₂ regeneration, indicating the importance of O₂ regeneration for CH₄ conversion. The reduced CH₄ conversion can be partially ascribed to the decreased carbon deposition and CO₂ production (Figure 6.18(a) and (b)). However, the CO selectivity is significantly improved especially for the Ni-rich catalysts without O₂ regeneration (Figure 6.17(b)), resulting from limited CO₂ production and increased production of CO and H₂ from partial oxidation of CH₄ during stage I (Figure 6.18(b-d)). The H₂/CO ratio from CLSRM without O₂ regeneration is ~3 for Ni₂Al, Ni_{1.5}Fe_{0.5}Al and NiFeAl (Figure 6.18(e)), which match well with the theoretical value for steam reforming of CH₄. With O₂ regeneration, H₂/CO ratio for Ni-rich Ni₂Al and Ni_{1.5}Fe_{0.5}Al are reduced, because the lattice oxygen of the Ni species consumed via partial oxidation of CH₄ (H₂/CO = 2) could not be recovered with steam to produce H₂ in stage II. With higher Fe contents, the H₂/CO ratio also increases as a result of additional H₂ produced from iron steam process.

Figure 6.18 Carbon deposition and gas productivity on various Ni-Fe redox catalysts in CLSRM cycles with and without O_2 regeneration. (a) Carbon deposition, (b) CO_2 , (c) CO, (d) H_2 , and (e) the H_2/CO ratio.

6.2.6 Comparison with co-feeding reforming of CH_4 and steam

In conventional steam reforming process, CH_4 and steam are fed in parallel to the reactor. Co-feeding of CH_4 and steam was further performed to compare the performance with the looping reforming experiments. In Figure 6.17(a), it shows that the Ni-rich catalysts are very active for steam reforming of CH_4 based on co-feeding reforming. CH_4 conversion reaches 97% for both Ni_2Al and $\text{Ni}_{1.5}\text{Fe}_{0.5}\text{Al}$ and decreases with increase in Fe contents, probably due to the reduced amount of metal surface for CH_4 activation, as indicated by the lowered solid conversion of the catalysts (Figure 6.19). But the selectivity to CO is limited to below 60% in co-feeding reforming (Figure 6.17(b)), as a result of the water gas shift reaction that converts CO and H_2O

to CO₂ and H₂. The result is in accordance with the reported performance of Ni-based catalysts in steam reforming of CH₄ [150, 151]. For the gas productivity (Figure 6.20), the productivity of CO₂ is lower in looping reforming as compared to co-feeding reforming for Ni-rich catalysts, and syngas productivity is related to CH₄ conversion. Therefore, it demonstrates that single Ni-based catalyst is promising for H₂ production from steam reforming of CH₄ through co-feeding reforming, while binary Ni-Fe catalysts are active for syngas production.

Figure 6.19 Solid conversion of Ni-Fe redox catalysts in looping and co-feeding reforming.

Figure 6.20 Comparison of gas productivity per cycle in co-feeding and looping reforming. (a) CO, (b) CO_2 , (c) H_2 and (d) H_2/CO ratio.

Figure 6.21 Cyclic gas productivity and CH_4 conversion on NiFeAl in CLSRM cycles with (cycles 31-60 and 91-120, solid symbols) and without (cycles 1-30 and 61-90, hollow symbols) O_2 regeneration.

6.2.7 Cycling stability in CLSRM

Besides catalytic activity, cycling stability of the redox catalyst in CLSRM is also an important consideration for practical applications. NiFeAl was selected to study the cycling stability in CLSRM with and without O₂ regeneration. As depicted in Figure 6.21, the performance of NiFeAl in the first 30 cycles without O₂ regeneration is less stable as compared to the one with O₂ regeneration, suggesting the necessity of O₂ regeneration to stabilize the chemical properties of the catalyst in the redox cycles. After regenerating the catalyst with O₂, in the subsequent cycles (no. 61-120), stable performances could be achieved on NiFeAl for both CLSRM with and without O₂ regeneration. However, CH₄ conversion in cycles 61-90 without O₂ regeneration is clearly lower than the cycles with O₂ regeneration. From the gas molar fraction as shown in Figure 6.22, it is found that the CO₂ fraction in both reduction and steam oxidation for CLSRM without O₂ regeneration is lower as compared to the one with O₂ regeneration, indicating reduced CO₂ selectivity. The decreased CO₂ production in reduction can be explained by the reduced amount of active lattice oxygen in the redox catalyst for complete combustion, while the reduced CO₂ production in steam oxidation may result from decreased activity of the reduced NiFeAl for water gas shift reaction. In one complete cycle, the fraction of CO and H₂ are similar for both CLSRM with and without O₂ regeneration (Figure 6.22(c)). Therefore, it can be concluded that higher selectivity to syngas and greatly reduced selectivity to CO₂ can be achieved on NiFeAl in CLSRM without O₂ regeneration. From Figure 6.22(d), it can be found that although the selectivity to carbon without O₂ oxidation is lower than

that with O₂ oxidation, the higher selectivity to CO in stage I still renders a higher overall CO selectivity in a complete CLSRM cycle without O₂ regeneration.

Figure 6.22 Gas molar fraction and selectivity on NiFeAl in CLSRM with and without catalyst regeneration with O₂. Gas molar fraction during (a) CH₄ reduction, (b) steam oxidation and (c) the complete cycle. (d) The selectivity of CO, CO₂, H₂ and C during reduction of NiFeAl. Solid and hollow symbols represent the cycles with (cycles 31-60 and 91-120) and without (cycles 1-30 and 61-90) catalyst regeneration with O₂, respectively.

6.2.8 Ni-Fe interaction in looping cycles

In CLSRM cycles, the redox catalysts are repeatedly reduced and oxidized. Thus, the phase composition shall influence the properties of the solid in each reaction stage.

For freshly prepared catalysts, spinel is present for all Ni containing catalysts, while only Fe_2O_3 is detected in Fe_2Al . The weak intensity of Fe_2O_3 in Fe_2Al suggests strong interaction between Fe species and the alumina support. During reduction with 5 vol.% CH_4/N_2 , lattice oxygen is consumed, accompanied with the appearance of metallic Ni and NiFe alloy in reduced catalysts (Figure 6.23(a)). Figure 6.23(b) reveals a clear peak shift to lower diffraction angles with higher Fe content in the catalysts, confirming the formation of NiFe alloy. Besides, graphited carbon was also detected in reduced NiFeAl (Figure 6.23(a)), with carbon filaments clearly observable in the SEM images (Figure 6.24). For Fe-rich catalysts, both FeO and Fe-rich NiFe alloy were detected in reduced $\text{Ni}_{0.5}\text{Fe}_{1.5}\text{Al}$ (Figure 6.25(a)), while only FeO was found in reduced Fe_2Al without any obvious peaks from metallic Fe (Figure 6.25(b)). Deep reduction of iron oxides to metallic Fe was limited in $\text{Ni}_{0.5}\text{Fe}_{1.5}\text{Al}$ and Fe_2Al , possibly due to the isomorphous replacement effect [152]. The XRD analysis results are in accordance with the calculated solid conversion of the catalysts in stage I (Figure 6.26(a)), which shows decreased solid conversion with higher Fe content at certain temperature (800 - 900 °C). The lower solid conversion of Fe_2Al contributes to the inferior CH_4 conversion and carbon deposition was also hindered due to the presence of FeO (not metallic Fe). Besides, higher Ni content in the binary catalysts could also lead to better reactivity with CH_4 , as indicated by the reduction curves as displayed in Figure 6.27. After steam oxidation, the peaks of metallic Ni remained (Figure 6.23) for Ni_2Al , indicating poor reactivity of metallic Ni with steam. The high valence Ni species are thus recovered during stage III with O_2 oxidation. On the contrary, Fe is

very active with steam to produce H_2 , which favors solid conversion during steam oxidation (Figure 6.26(b)). It is noteworthy that NiFeAl exhibits high solid conversion during steam oxidation at low reaction temperatures (700 and 750 °C), recognizing its excellent reactivity with steam. As shown in Figure 6.23(a), spinel phase appears in steam oxidized $Ni_{1.5}Fe_{0.5}Al$ and NiFeAl, evidencing the oxidation of Fe by steam. It can be found that the peak of NiFe alloy shifts to higher diffraction angles after steam oxidation for $Ni_{1.5}Fe_{0.5}Al$ and NiFeAl, suggesting that Fe segregates from the alloy phase, leaving Ni still in the metallic state. For Fe_2Al , only spinel phase is detected in steam oxidized sample, which can be assigned to the Fe_3O_4 - $FeAl_2O_4$ solid solution (Figure 6.25(b)). The formation of Fe_3O_4 - $FeAl_2O_4$ spinel solution is resulted from isomorphous replacement of Fe^{3+} with Al^{3+} in Fe_3O_4 grains. The replacement effect is limited in $Ni_{0.5}Fe_{1.5}Al$ with separated spinel phases (Fe_3O_4 and $FeAl_2O_4$) being partially recovered after steam oxidation, and the Fe-rich alloy changes to a Ni-rich one, as indicated by the peak shift to higher diffraction angles (Figure 6.25(a)).

Figure 6.23 Phase evolution of the Ni-Fe redox catalysts in CLSRM cycle. (a) XRD patterns of reduced and steam oxidized catalysts. (b) Enlarged peak of the NiFe alloy at 43°~45° in (a).

Figure 6.24 SEM images of reduced catalysts after stage I. (a) $\text{Ni}_{1.5}\text{Fe}_{0.5}\text{Al}$ and (b) NiFeAl .

Figure 6.25 XRD patterns of reduced and steam oxidized catalysts. (a) $\text{Ni}_{0.5}\text{Fe}_{1.5}\text{Al}$, (b) Fe_2Al , and (c) standards of the spinel phases, iron oxides and FeNi alloys.

Figure 6.26 Solid conversion of various Ni-Fe redox catalysts during different reaction stages. (a) 5 vol.% CH_4/N_2 reduction and (b) steam and O_2 oxidation.

Figure 6.27 Solid conversion of various Ni-Fe redox catalysts during reduction with 5 vol.% CH_4/N_2 as a function of reduction time in the 30th cycle.

6.3 Summary

In summary, a series of Ni-Fe redox catalysts with varying Ni/Fe ratios were designed and applied in CLSRM. It was found that carbon deposition from catalytic CH₄ decomposition on reduced catalysts in the reduction stage played an important role on the conversion of CH₄. In the subsequent steam oxidation stage, the deposited carbon was selectively gasified to syngas with CO selectivity as high as 95%. In typical reforming cycles, high CH₄ conversion up to 97.5%, high CO selectivity up to 92.9%, and high productivity of CO (9.6 mol kg⁻¹) and H₂ (29.0 mol kg⁻¹) per cycle could be achieved at 900 °C on the binary Ni-Fe catalyst with equimolar Ni and Fe with outstanding cycling stability.

Chapter 7 Conclusions and Future Perspectives

7.1 Conclusions

CLC has advantages of inherent carbon capture, reduced NO_x formation as well as increased thermodynamic efficiency over conventional combustion. Applying the chemical looping concept, various fuel conversion processes was established for combustion, reforming and selective oxidation, etc. The successful implement of these processes highly relies on the development of the oxygen carrier or redox catalyst, in which both the bulk and surface properties play fundamental roles on the stepwise reactions. It is desirable to study the interaction of the components in the oxygen carrier under chemical looping conditions to provide knowledge for the design of high-performance oxygen carrier. In this thesis, Mg, Cu, and Fe modification of the Ni-based, Al_2O_3 -supported oxygen carriers were investigated. The main findings are summarized as follows.

MgO , Al_2O_3 and MgAl_2O_4 have been used as support material for Ni-based oxygen carriers. At high temperature above 800°C , interaction between NiO and MgO , Al_2O_3 will form $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ solid solution and NiAl_2O_4 spinel, which will lower the activity for NiO . The work in Chapter 4 investigated the effect of MgO modification on the $\text{NiO}/\text{Al}_2\text{O}_3$ oxygen carrier. The oxygen carriers were prepared by a co-precipitation method with urea to obtain Ni-Mg-Al LDH as the precursors, followed by calcinations. The oxygen carriers were subjected to the 100 chemical

looping cycles with 5 vol.% H_2/N_2 and 5 vol.% O_2/N_2 , to investigate the oxygen transfer capacity and reduction/oxidation kinetics over cycles. An activation period presented for the Mg modified oxygen carriers (Ni_2MgAl , $\text{Ni}_{2.5}\text{Mg}_{0.5}\text{Al}$), while it was absent for the pristine $\text{NiO}/\text{Al}_2\text{O}_3$ oxygen carrier (Ni_3Al). Material characterization and analysis by XRD and H_2 -TPR revealed the coexistence of halite (MgO-NiO) and spinel ($\text{MgAl}_2\text{O}_4\text{-NiAl}_2\text{O}_4$) solid solutions, and a net migration of Ni^{2+} from the spinel phase to the halite phase was observed after the chemical looping tests. The composition change over cycles determined the performance of the oxygen carriers. It showed that MgAl_2O_4 could not be considered as inert support for Ni-based oxygen carrier, and MgO modification benefited the sintering resistance of the oxygen carrier.

Although $\text{NiO}/\text{Al}_2\text{O}_3$ has good reactivity with CH_4 , the reaction is not selective towards combustion or partial oxidation, with severe carbon deposition on the O-depleted $\text{Ni}/\text{Al}_2\text{O}_3$ oxygen carrier. Cu-based oxygen carrier can provide selective oxygen for complete CH_4 combustion, but the sintering resistance was limited by the low melting point of Cu. In Chapter 5, a series of $\text{NiO-CuO-Al}_2\text{O}_3$ oxygen carriers were studied to explore the phase interaction in these oxygen carriers. The oxygen carriers were derived from Ni-Cu-Al LDH precursors, which were prepared via hydrothermal syntheses using urea as the precipitant. It was found that formation of NiAl_2O_4 was favored over CuAl_2O_4 via compositions analysis by TGA and SXRD. SXRD revealed the mixing of NiO and CuO , and the resulted enhanced lattice oxygen activity in both oxides was observed in H_2 -TPR. However, the lattice oxygen activity in the spinel phase was reduced due to the formation of stable solid solution

$\text{Ni}_{1-x}\text{Cu}_x\text{Al}_2\text{O}_4$, which appears to be an excellent retardant for carbon deposition.

Fe-based oxygen carrier received considerable attention in chemical looping due to its abundance, low cost and environment friendly characters. In Chapter 6, a series of Ni-Fe- Al_2O_3 redox catalysts were designed and investigated in chemical looping steam reforming of CH_4 . During the reduction with 5 vol.% CH_4/N_2 , severe carbon deposition was observed for the Ni-containing samples. The deposited carbon was purposely used to produce syngas in the next steam gasification step, followed by O_2 regeneration. It was demonstrated that CO selectivity was significantly enhanced through the stepwise reactions compared to conventional co-feeding reforming, achieving up to 92.9% at 900 °C with the optimized equimolar Ni and Fe redox catalyst. The excellent performance of the Ni-Fe redox catalyst was resulted from the highly reactive Ni species for CH_4 activation, the reduced Fe species for water splitting, and the NiFe alloy in the reduced catalyst for catalytic CH_4 decomposition. This work showed that the thermodynamic equilibrium in steam reforming of CH_4 was successfully tuned by stepwise looping reforming to produce more CO by inhibiting the water gas shift reaction.

7.2 Future perspectives

The work in chapter 4 shows that the interaction of the active phase (NiO) with the support (MgAl_2O_4) could have important impact on the oxygen carrier performance in chemical looping cycles. The activity of lattice oxygen can be controlled by proper modification to fulfil the requirements for varied applications. For partial oxidation of

CH₄, the selectivity to CO₂ should be inhibited for more CO production. In this case, the oxygen activity in the oxygen carrier should be lowered to prevent from producing CO₂ even when the oxygen to fuel ratio is high. In Chapter 4, MgO modification on NiO/Al₂O₃ resulted in reduced oxygen donating kinetics in the reduction and improved regeneration activity in the oxidation. It is suggested to study the effect of MgO modification on CuO/Al₂O₃, which may achieve good CO selectivity with lower carbon deposition compared to NiO/Al₂O₃. In Chapter 5, it was found that the Ni_xCu_{1-x}Al₂O₄ spinel solid solution had lower activity than NiAl₂O₄ and CuAl₂O₄, which showed good carbon resistance. Ni_xCu_{1-x}Al₂O₄ spinel solid solution may offer improved CO selectivity, in which the loading of Ni, Cu oxides and the ratio of Ni/Cu should be further optimized.

In Chapter 6, chemical looping steam reforming of CH₄ was coupled with CH₄ decomposition catalyzed by the NiFe alloy in the reduced oxygen carrier, resulting in improved syngas selectivity and productivity. The collaboration between the reducible lattice oxygen and the active catalytic sites may significantly improve the performance of chemical looping processes. For example, if catalytic sites for propane dehydrogenation involves in chemical looping dehydrogenation of propane, the lattice oxygen can consume the H₂ and shift the reaction to propene, with enhanced propane conversion. However, the selectivity to the alkenes may be decreased if the oxygen activity in the oxygen carrier is too much high that it would promote combustion. Low selectivity to ethylene was reported with Mn/MgO catalyst [35]. To get a balanced performance in conversion and selectivity, the oxygen carrier needs careful

optimization with promoters or mixed oxides so that the lattice oxygen activity could be tailored for selective removal of H_2 in chemical looping dehydrogenation of propane/ethane. Typical catalysts for dehydrogenation of ethane and propane are based on chromia-alumina or Pt, while supported vanadium oxide and molybdenum oxide have been extensively researched in oxidative dehydrogenation of propane and ethane [153, 154].

At high temperature chemical looping processes, the lattice oxygen in the bulk of oxygen carrier is transferred in the stepwise reactions. Beyond that, the property of the surface oxygen may have dominating effects in low temperature chemical looping processes. One example is that selective anaerobic oxidation of CH_4 over a copper-exchanged mordenite zeolite can directly synthesize methanol. It was reported that after activation in helium at 673 K, consecutive catalyst exposures to 7 bars of CH_4 and then water at 473 K, could consistently produce 0.204 mole of CH_3OH per mole of copper in zeolite [37]. However, the performance is highly affected by the reaction condition, i.e. activation temperature and time, CH_4 pressure, and the Cu loading in the catalyst as well [37, 155]. Considered that this reaction is not thermodynamically favoured, it also inevitably needs much energy to put it forward. Although CH_4 to methanol conversion is a novel processes, more research is desirable on the catalyst design and process optimization to make it possible for industry implement.

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Appendix

List of abbreviations

CLC	Chemical Looping Combustion
LDH	Layered Double Hydroxides
CCS	Carbon Capture and Storage
SEM	Scanning Electron Microscopy
XRD	Powder X-Ray Diffraction
TPR	Temperature Programmed Reduction
TPO	Temperature Programmed Oxidation
SXRD	Synchrotron X-Ray Powder Diffraction,
TGA	Thermogravimetric Analysis
SRM	Steam Reforming of Methane
CLSRM	Chemical Looping Steam Reforming of Methane
ΔG	Change of Gibbs Free Energy
CLOU	Chemical Looping with Oxygen Uncoupling
BET	Brunauer–Emmett–Teller
RALO	Redox-Active Lattice Oxygen
OTC	Oxygen Transfer Capacity

Publications

- [1] J. Huang, W. Liu, Y. Yang, Phase interactions in Mg-Ni-Al-O oxygen carriers for chemical looping applications, Chem. Eng. J. 326 (2017) 470-476.
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