Use of Spinel Nickel Aluminium Ferrite as Self-Supported Oxygen Carrier for Chemical Looping Hydrogen Generation Process

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ABSTRACT

Chemical looping hydrogen generation (CLHG), as a new technology involved in chemical looping combustion (CLC) process and steam-iron process, has attracted attention for clean energy generation and efficient energy conversion. A systematic investigation of spinel NiFeAlO$_4$ has led to characterization of a well-defined self-supported oxygen carrier which was prepared by solid state reaction. The redox behavior of NiFeAlO$_4$ shows the enhancement on the resistance to agglomeration exceeding previously reported CLC process using similar compositions including Fe$_2$O$_3$, NiO and NiFe$_2$O$_4$ without any inert support. Moreover, the high CO$_2$ conversion and H$_2$ generation by NiFeAlO$_4$ oxygen carrier under a fixed-bed reactor (FxBR) were obtained. The reaction mechanism of NiFeAlO$_4$ subjected to the isothermal stepwise reduction in a sequence of varying durations by XRD was also demonstrated, which provided with a novel function of self-supported and agglomeration-resistant characteristic in the oxygen carrier system.

Keywords: Chemical looping hydrogen generation; Oxygen carrier; NiFeAlO$_4$; Spinel; Redox behavior.

INTRODUCTION

The increase in concentration of greenhouse gases (GHG) has caused global warming, in which CO$_2$ GHG is considered the primary contribution in the environment as a result of the fossil fuels combustion (Herzog et al., 2000; Figueroa et al., 2008). Chemical looping combustion (CLC) process has emerged as an attractive option to generate power with accomplishing the inherent CO$_2$ capture by the oxygen carrier which was carried out in the two interconnected reactors, an air reactor and a fuel reactor. During the operation in the CLC process, metal oxide (Me$_x$O$_y$) as oxygen carrier provides the oxygen sources (oxygen capacity) for a combustion reaction, instead of air, thereby avoiding direct contact between fuel and air (Richter et al., 1983; Fang et al., 2009; Egmond and Hekkert, 2012). The fuels are converted to CO$_2$/steam gases and produce high-grade heat to the steam engine for electricity generation (Ekstrom et al., 2008; Chiu and Ku, 2012). Additionally, a potential energy conversion technology, chemical looping hydrogen generation (CLHG), was proposed using the chemical looping combustion process integrated with the steam-iron process, which is composed of a fuel reactor, a steam reactor and an air reactor, as shown in Fig. 1 (Jozwiak et al., 2007; Kang et al., 2010; Wang et al., 2012; Cho et al., 2014; Cao et al., 2014).

In CLHG process, oxygen carriers such as iron oxide (Fe$_2$O$_3$) move through the fuel reduction, steam oxidation and air oxidation in sequence. Initially, for example, syngas as the fuel is introduced into the fuel reactor and reduced the oxygen carrier to form the metal (Me), and then produced outlet gases of CO$_2$ and steam as depicted in Eq. (1). Then, H$_2$ gas is generated by the oxidation of Me by steam (Eq. (2)), and subsequently oxidized to the original oxide phase by oxygen gas in air reactor (Eq. (3)).

Outlet gases from the air reactor contain N$_2$ and unreacted oxygen gases. Thus, the primary benefit of CLHG process is combined CO$_2$ separation and H$_2$ generation without entailing any direct cost or energy penalty (Adánez et al., 2012; Moldenhauer et al., 2012).

\[
\frac{\nu}{2} \text{CO} + \frac{\nu}{2} \text{H}_2 + \text{Me}_x\text{O}_y \rightarrow \frac{\nu}{2} \text{CO}_2 + \frac{\nu}{2} \text{H}_2\text{O} + x\text{Me} \quad (1)
\]

\[
x\text{Me} + (y-1)\text{H}_2\text{O} \rightarrow x\text{Me}_x\text{O}_{y-1} + (y-1)\text{H}_2 \quad (2)
\]

\[
\text{Me}_x\text{O}_{y-1} + \frac{1}{2} \text{O}_2 \rightarrow \text{Me}_x\text{O}_y \quad (3)
\]

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Therefore, redox behaviour of an oxygen carrier is a key issue for the use in CLHG process (Adánez et al., 2004; Cho et al., 2004; Hossain et al., 2008; Kang et al., 2010). In our previous study, nickel ferrite (NiFe₂O₄) powder with a single spinel phase demonstrated higher redox behaviour than standard nickel oxide (NiO) and iron oxide (Fe₂O₃) by a thermogravimetric analyzer (TGA). However, the agglomeration phenomenon of reduced state of prepared oxygen carriers with a low thermal stability under high reaction temperature is considered to be the main concerns to degrade their multi-redox cycling behaviour in the CLC process (Lambert et al., 2011; Kuo et al., 2013; Chiu et al., 2014; Tseng et al., 2014). The addition of Al₂O₃ as inert support in NiFe₂O₄ system was preliminary investigated, while the formation of new spinel phase of nickel aluminium ferrite (NiFeAlO₄) was obtained. A noteworthy result from the Ni/Fe/Al triad data, Al³⁺ ions significantly promote the catalytic activity of mixed metal oxide containing Ni and Fe. The Ni/Fe-based oxides with Al³⁺-containing composition showed much higher activity than the monometallic Ni and Fe oxides, as well as Ni/Fe binary oxides (Gerken et al., 2012; Gerken et al., 2014; Zhang et al., 2015). In this study, the synthesis of spinel NiFeAlO₄ as oxygen carrier by simple solid state reaction and reaction mechanism of NiFeAlO₄ are primarily discussed. Notably, the CO₂ conversion and H₂ generation performed by a fixed-bed reactor (FxBR) system are also investigated for the application of CLHG process in this study.

EXPERIMENTS

Preparation of NiFeAlO₄ Powder

For the preparation of NiFeAlO₄, a stoichiometric mixture of commercial oxides, NiO, Fe₂O₃, and Al₂O₃, was physically mixed and ground at room temperature for 2 hrs in ethyl alcohol using high-energy ball milling in a planetary ball mill (Model PM100, Retsch, GmbH, Germany). The mixture powder and zirconium balls were sealed in a 50 mL zirconium oxide grinding jars using ball-to-powder and solvent-to-material weight ratios of 5:1 and 2:3, respectively. The rotation speed of the sun wheel was maintained at 380 rpm. The obtained slurry was dried in a vacuum evaporator at 60°C, whereupon the dry powder was calcined at 380°C for 2 hr to form the NiFeAlO₄ phase.

\[
2\text{NiO} + \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 \rightarrow 2\text{NiFeAlO}_4
\]  (4)

The crystalline structure of the prepared sample was verified by X-ray diffraction (XRD, Bruker D2 Phaser) using Cu-Kα radiation source (λ = 1.5405 Å), employing a scanning rate of 0.02° per second in the 2θ range from 20° to 80°. The microstructure and particle size of oxygen carrier were examined using field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6500F).

Redox Cycling Investigation

In order to simulate the redox behaviour of the prepared NiFeAlO₄ in the CLC process, Netzsch STA 449-F3 TGA was used to monitor the weight change of the sample and was measured isothermally as a function of time under reducing and oxidizing atmospheric environments, respectively. The reaction mechanism of the oxygen carrier during the redox cycling test was determined by the XRD analysis at different reduction time. The stability performance and agglomeration-resistance of oxygen carriers were investigated by ten redox cycles, in which each cycle was performed by 20 min reduction and 5 min oxidation. For all experiments in a TGA system, 200 mg fresh oxygen carrier was loaded into an alumina crucible and heated to 900°C with the heating rate...
of 10 °C min⁻¹ in N₂ gas. The fuel flow (200 mL min⁻¹) composed of 10% CO, 10% H₂ and 80% N₂ gases was used for the reduction period, and air flow (200 mL min⁻¹) was used for the oxidation period, respectively. To avoid mixing of fuel and air gases, the system was flushed by pure N₂ gas with a flow rate of 200 mL/min for 5 min after each reducing and oxidizing period.

Experimental Setup and Procedure in Fixed-Bed Reactor

The ability of CO conversion and H₂ generation of prepared NiFeAlO₄ oxygen carrier were carried out in a laboratory-scaled FxBR system. The scheme of the experimental setup used in this study is shown in Fig. 2, and consisted of a single stainless steel tube in a split tube muffle furnace with an inner diameter of 25.4 mm and a bed height of 200 mm in heating section. The temperature was measured and controlled by the thermocouple within the reactor and operated at 900°C where 1.2 g of NiFeAlO₄ oxygen carrier was placed. Diluted CO gas (20% CO and 80% N₂) was used as fuel for reduction at a flow rate of 500 mL min⁻¹ for 60 min. After the reducing period was completed, the system was purged with N₂ gas, and steam gas was introduced at an injection rate of 210 mL min⁻¹ for 120 min controlled by a syringe pump (KD Scientific KDS100) for the generation of H₂ gas by water-splitting. The outlet gases from the reactors were cooled by a cold trap and analyzed by gas chromatography equipped with a non-dispersive infrared analyzer (NDIR, Molecular Analysis 6000i) and hydrogen sensor to detect the concentration of outlet gases, including CO₂, CO and H₂.

RESULTS AND DISCUSSION

NiFe₂O₄ is a spinel oxide with the strongest diffraction peak of (311) plane recorded at a 2θ of 35.70° that has been studied previously as an oxygen carrier for CLC/CLHG process (Kuo et al., 2013). Fig. 3 shows the XRD patterns of the NiFeAlO₄ powder synthesized by solid state reaction and calcined at 900–1300°C. By the wide-range scan shown in Fig. 3(a), the crystallite structure of the prepared NiFeAlO₄ at 900°C possessed separate phases of NiFe₂O₄, NiO and Al₂O₃. As increasing over 1100°C, the NiAl₂O₄ solid solution was formed due to the interdiffusion of NiO and Al₂O₃ with the enhanced kinetics provided by the higher temperature. As increasing over 1300°C, the diffraction patterns revealed a single cubic-spinel NiFeAlO₄ phase without any existence of the secondary phase, which was verified the NiFeAlO₄ formed by Al³⁺ ions within the NiFe₂O₄ crystal lattice.

Fig. 2. Schematic diagram of the FxBR system for chemical looping hydrogen generation process.
Fig. 3. Systematic phase evolution of NiFeAlO$_4$ powder prepared at different calcination temperatures (a) wide-range scan, (b) partial scan at a smaller scanning rate.

Fig. 3(b) shows the XRD patterns of the prepared samples, where (311) peak at a scan range of 35.0° to 37.5° is shown in expanded form to understand the variation of lattice constant (a$_0$) with the peak shift at different calcination temperatures. The obtained diffraction angle ($2\theta$) of the samples calcined at 900°C is close to the reported value of NiFe$_2$O$_4$ (JCPDS-10-0325). As increasing calcination temperature over 1200°C, the diffraction angle apparently shifted to a higher value, in which the interdiffusion of all oxide powders occurred to form spinel NiFeAlO$_4$ phase. It can be attributed to the replacement of Fe$^{III}$ ions with a larger ionic radius of 0.65 Å by a smaller ions radius of Al$^{III}$ (0.53 Å) ions within the original NiFe$_2$O$_4$ lattice.

From the XRD result, the crystal size of the NiFeAlO$_4$ calcined at 1300°C was calculated from the broadening in the diffraction peak, employing the Debye-Scherrer formula. The size of crystals was calculated for different preferred planes with an average value of approximately 100 nm. However, the agglomeration of prepared NiFeAlO$_4$ at 1300°C with well-defined crystalline structure was distributed in the size range of 100–300 nm in Fig. 4(a), indicating that the high surface energy among the particles provided strong interactions (such as van der Waals forces) (Rance et al., 2010).

Fig. 4(b) shows the redox cycling test by syngas for 150-min reduction period and by air for 30-min oxidation period at 900°C in a TGA. The corresponding XRD pattern of NiFeAlO$_4$ subjected to the isothermal stepwise reduction in a sequence of varying durations was displayed in Fig. 4(c). For the reduction period at 20 min, the peak at 43.99° belonging to Fe(Ni) appeared, while the Fe(Ni) concentration increased with the reduction time up to 90 min. Finally, the oxygen carrier was completely reduced at 120 min with the separate phases of Fe(Ni) and Al$_2$O$_3$. In the oxidation period, only NiFeAlO$_4$ peaks were observed, indicating that the Fe(Ni) and Al$_2$O$_3$ could be oxidized back to the original phase at 900°C. Interestingly, the reduction profile of NiFeAlO$_4$ can be roughly divided into three stages. In the initial stage, the observed minor Fe(Ni) and Al$_2$O$_3$ can be mainly attributed to the reduction of NiFe$_2$O$_4$. The transition stage to the final stage corresponded to a complete reduction process, which gave rise to major products of Fe(Ni) and Al$_2$O$_3$. The reduced state of NiFeAlO$_4$ oxygen carrier obtained in the final reduction stage whose inner core consists of Al$_2$O$_3$ as inert support evidently improved the thermal stability due to the promising self-supported function in oxygen carrier system. Ishihara and Zhong (2011) reported that the microstructure of Fe(Ni) bimetal possessed high porosity, and large triple phase boundary (TPB) area was proved to prevent the agglomeration of particles, as compared to Fe and Ni monometals. Consequently, the larger TPB area of Fe(Ni)/Al$_2$O$_3$/O$_2$(air) system in the oxidation period was beneficial to fully restore back to the original NiFeAlO$_4$ phases at 900°C. However, as compared to traditional oxygen carriers using Al$_2$O$_3$ as the support, interdiffusion-induced compound with a less reactivity, such as Ni$_2$Al$_2$O$_5$ in NiO/Al$_2$O$_3$ system, was formed, which substantially decreased the oxygen capacity of oxygen carriers during the reduction period in the CLC process (Gayán et al., 2011). It is reasonable to predict that the NiFeAlO$_4$ powder calcined at 1100°C with the existence of NiAl$_2$O$_4$ was infeasible to be used as the oxygen carrier in the CLC process. Therefore, the calcined temperature exceeded 1300°C enhanced kinetics for Al$^{III}$ ions within the NiFe$_2$O$_4$ crystal lattice to form the spinel NiFeAlO$_4$ phase. From the aforementioned results, self-supported spinel NiFeAlO$_4$ oxygen carrier with the agglomeration resistance in fuel/air reactors is suggested as a feasible material for the CLC process.

To evaluate the multi-redox cycling behavior of NiFeAlO$_4$ as oxygen carrier in the CLC process, the weight variation and the reaction rates versus cycle numbers at 900°C were performed, shown in Figs. 5(a) and 5(b) The reaction rates
Fig. 4. (a) SEM image of prepared NiFeAlO$_4$ powder, (b) weight change and (c) XRD patterns as a function of reaction time for a single redox test.

(dW/dt, % min$^{-1}$) at different weight variations (W%) under reduction and oxidation periods were calculated by differentiating the data. NiFeAlO$_4$ spinel powder exhibited a quite stable redox activity without apparent degradation after ten cycles, while the reduction and oxidation rates were fairly stable without variation. To be noted, however, the reduction rate was low for the first cycle mainly arose from the fresh oxygen carrier with a compact layer in the outer surface. After the first cycle, the apparent pores inside the samples were generated, which favors stabilizing the reduction rates (1.78 % min$^{-1}$) and oxidation rates (2.95 % min$^{-1}$), respectively (Zhang et al., 2012).

Fig. 6(a) shows the concentrations of outlet gases as a function of reaction time for NiFeAlO$_4$ at 900°C in the FxBR system. The hydrocarbon gases including CO and CO$_2$ were introduced at the beginning with an approximate 6 min time delay for the gas measurement. The concentration of CO$_2$ gas rose rapidly in the reduction period which was evidently proved the propensity of NiFeAlO$_4$ oxygen carrier to convert CO into CO$_2$. The conversion efficiency of CO ($\gamma_{co}$) and the degree of mass-based conversion of the oxygen carrier ($\omega$) for different lengths of reduction stage NiFeAlO$_4$ are depicted in Fig. 6(b). The values of $\gamma_{co}$ and $\omega$ are defined as the fraction of CO$_2$ divided by the sum of the fractions of carbon containing gases in the outlet gases and the mass of the oxygen carrier in its fully oxidized state by using Eqs. (5)–(6), respectively.

\begin{align}
\gamma_{co} &= \frac{x_{co2, out}}{x_{co2, out} + x_{co, out}} \\
\omega &= \frac{m}{m_{ox}}
\end{align}

where $x_{co2, out}$ and $x_{co, out}$ are the fractions of CO$_2$ and CO in the outlet gases, obtained from measured volumetric flow rate in the gas analyzer. Therefore, the $\gamma_{co}$ value approaching 1.0 corresponds to total conversion of the carbon monoxide to carbon dioxide. $m$ is the mass of the oxygen carrier, and $m_{ox}$ denotes the mass of the oxygen carrier with oxidized state. In our study, the value of $\omega$ at 1.0 is the beginning of each reduction period. It is noteworthy that the conversion of CO was fairly constant at around 0.9. The change in $\omega$ for NiFeAlO$_4$ oxygen carrier decreased by performing experiments with extending the length of the reduction. It is also concluded that the NiFeAlO$_4$ oxygen carrier has an excellent conversion of CO with the initial reduction stage.

Interestingly, the complete reduction of the NiFeAlO$_4$ as oxygen carrier comprised Fe(Ni) alloy with Al$_2$O$_3$ inert support. Optimistic results have previously demonstrated that Fe(Ni) from reduced Ni-ferrites could be utilized as
Fig. 5. Multi-redox cycling behaviors of NiFeAlO$_4$ system under syngas (reduction) and air (oxidation) environments at 900°C (a) weight loss, (b) reaction rates.

Fig. 6. (a) Concentrations of outlet gases as a function of reaction time and (b) the conversion of CO ($\gamma_{CO}$) as a function of mass-based conversion of the oxygen carrier ($\omega$) for the NiFeAlO$_4$ at 900°C.
reducing agent in the steam-iron process for H$_2$ production; therefore, CLHG process may be a practical application of NiFeAlO$_4$ oxygen carrier (Kuo et al., 2013). To test the decomposition of steam to H$_2$, steam gas was introduced into the reactor at 900°C. Fig. 7 shows the concentration of H$_2$ gases from the steam decomposition using reduced NiFeAlO$_4$ oxygen carrier. Within 5 min, a maximum H$_2$ concentration of 7.6 mL min$^{-1}$ was obtained. Thus, reduced NiFeAlO$_4$ oxygen carrier demonstrated the feasibility to decompose steam into H$_2$. After 60 min, the accumulated volume of H$_2$ gas remained at a constant value of 103.5 mL, indicating that the reduced NiFeAlO$_4$ oxygen carrier was completely oxidized with steam to a mixture phase of Ni, Fe$_3$O$_4$ and Al$_2$O$_3$. Conversely, reduced nickel oxides or nickel metals are intrinsically less capable of water-splitting, which is consistent with the equilibrium phase diagrams of the syngas redox process (Gupta et al., 2007; Li et al., 2009).

From the above-mentioned discussion, a schematic mechanism of the redox reaction pathway for prepared NiFeAlO$_4$ powder as oxygen carrier under the three reactors in CLHG process has been accordingly proposed, depicted in Fig. 8. In the fuel reactor, the mixture phases of Fe(Ni) and Al$_2$O$_3$ were progressively formed during the consecutive reduction stages as it is released from the NiFeAlO$_4$ oxygen carrier. Subsequently, the reduced NiFeAlO$_4$ comprised major Fe(Ni) was capable of promoting the H$_2$ generation by steam-iron process and the agglomeration resistance in the oxidation period. After the steam reactor, the generated mixture phase of Ni, Fe$_3$O$_4$ and Al$_2$O$_3$ was evidently proved to be oxidized to the origin phase in the air reactor. Therefore, NiFeAlO$_4$ as self-supported oxygen carrier is suggested a promising material for the application in CLHG process.

CONCLUSIONS

In summary, solid state reaction was used to prepare a potential self-supported oxygen carrier for CLHG process. Systematic investigation of these materials has led to the
characterization of a well-defined NiFeAlO₄ spinel structure, in which the structural change by AlIII substitution into the spinel lattice was verified. The reaction mechanism for self-supported NiFeAlO₄ oxygen carrier under the redox process has been accordingly proposed from the results of XRD and TGA. By ten redox cycling tests at 900°C, NiFeAlO₄ oxygen carrier with the promising performances of self-supported function and agglomeration resistance was recognized as a potential oxygen carrier. In addition, NiFeAlO₄ oxygen carrier with high CO₂ conversion and H₂ generation has been proved in FxBR.

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