



Full Length Article

Determination of redox pathways of supported bimetallic oxygen carriers in a methane fuelled chemical looping combustion system

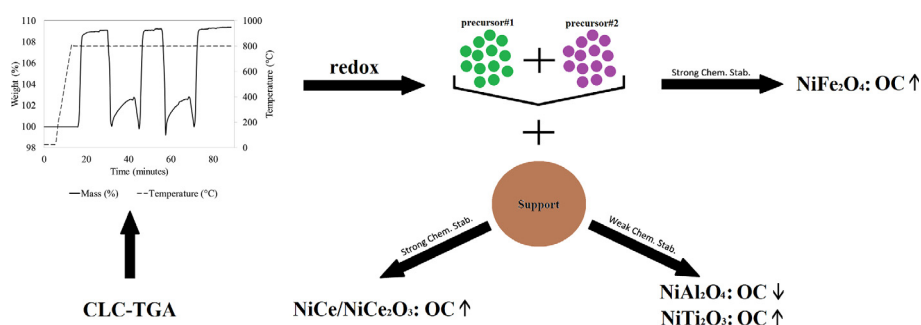


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GRAPHICAL ABSTRACT



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ABSTRACT

The incipient wetness impregnation technique was used to synthesize supported bimetallic precursors (Ni and Co, Cu or Fe) by Al₂O₃, CeO₂, TiO₂ and ZrO₂ in order to understand both oxidation and reduction reactions (redox) pathways during the methane chemical looping combustion (CH₄-CLC). Understanding the reaction pathways helps to enable proper modifications of oxygen carriers, which later assists in choosing chemically stable precursors that could enhance the overall redox reaction rates. A higher solid conversion rate and fewer interactions with supports will produce highly reactive and thermally stable oxygen carriers. The BET surface area results showed highest increase in Ni-Fe/ZrO₂ sample by 17.73% and highest decrease in Ni-Fe/CeO₂ sample by 78.80%. The internal mass transfer results revealed that the reaction and internal diffusion for Ni-Fe/TiO₂ and Ni-Fe/ZrO₂ samples were similar; however, the effectiveness factor of the Ni-Cu/TiO₂ sample showed isothermal surface reaction was the controlling step. Under the operating condition presented in this study (oxidation with air at 20 ml/min, and reduction with CH₄ balanced with N₂ at 20 ml/min), most stable samples for CLC practical deployment were Ni-Co/ZrO₂, Ni-Cu/ZrO₂, and Ni-Fe/ZrO₂ due to their exhibition of stable oxygen transport capabilities, and nonexistence of interaction between precursors and supports.

1. Introduction

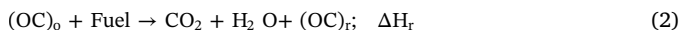
Global warming, nowadays, is caused by the large-scale emission of greenhouse gases. A large portion of emissions results from industrially emitted carbon dioxide [1]. Carbon capture and sequestration processes

are among the most promising strategies to decrease the atmospheric concentration of carbon dioxide. The oxy-fuel combustion process means that the fuels (gas or solid) are combusted with only oxygen. This process is considered clean where a mixture of CO₂ and H₂O is produced and easily separated while the formation of nitrogen oxides

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(NO_x) is avoided [2]. The Chemical Looping Combustion (CLC) process has great potential to become an efficient and clean alternative technology [2]. CLC was introduced as a means of reducing the CO₂ emission [3]. It was chosen among others because of its potential to reduce the cost of the CO₂ capture process by up to 50% [4]. In the CLC process, a solid oxygen carrier is oxidized at high temperatures inside a reactor called the air reactor. The reactants are air and the solid oxygen carrier, which is transferred to the fuel reactor. In the case of fixed bed reactors, the carrier is exposed to the fuel. Conversion of fuel and reduction of the oxygen carrier is then carried out. The process is then repeated in multiple cycles (i.e. oxidation/reduction reactions). The following reactions describe the general CLC process.



where OC is Oxygen Carrier; ΔH_o is enthalpy of oxidation reaction (J); ΔH_r represents enthalpy of reduction reaction (J); and r & o subscripts represent reduced and oxidized, respectively.

CLC of gaseous fuel (i.e. CH₄) is used to separate CO₂ from N₂ when gaseous fuel is combusted. The oxygen reacts with the gaseous fuel to produce end-products like CO₂ and H₂O. After the condensation of H₂O, a highly concentrated stream of CO₂ can be obtained. This process reduces the penalties (heat loss and CO₂ capture/separation unit) that are usually associated with the capture of CO₂ from flue gases resulted from the combustion of gaseous fuel in an air environment [5]. Although not all transition metals are suitable for oxygen carriers due to their reactivity, cost and/or environmental concerns, different attempts have been made to enhance the reactivity of some transition metals. Zheng et al. [6] studied different combinations of Cu as an active site, as well as SiO₂ and Al₂O₃ supports for their capability to produce a high concentration stream of H₂ in a fixed bed reactor (270 cm³). It was then reported that a 95% conversion of H₂ was observed at 500 °C. The carrier with 36.1% Cu loading was found to exhibit the highest oxygen capacity of 9%. Harper et al. [7] studied copper-based oxygen carriers in a packed bed reactor at 400 °C. It was found that mixing different copper oxides and oxygen carriers in the fuel reactor at a ratio of 1:6 (Al₂O₃) could prevent the agglomeration between the active site (Cu) and inert support (Al₂O₃) in the solid particles. It was concluded that the concentration of copper at the particle surface was proportional to the presence of agglomeration. Zhu et al. [8] investigated the use of Fe₂O₃/Al₂O₃ (3:2) in a newly proposed configuration of a CLC packed-bed reactor at 850 °C. High concentrations of H₂ (95 vol%) were achieved after 20 cycles of oxidation/reduction reactions. Hamers et al. [9] examined the effect of pressure (2–7.5 bar at 600 °C) on the performance of a NiO/CaAl₂O₄ oxygen carrier in a packed bed reactor. It was concluded that changes in pressure have a small effect on the outlet molar fractions of O₂ and H₂, which were observed in both oxidation and reduction cycles (8.75% and 12.5%, respectively). Song et al. [10] investigated the effect of temperature, gas flow rate, initial sample weight and particle size on a novel CaSO₄ oxygen carrier for methane combustion. It was found that a reaction temperature of 950 °C showed the highest methane reduction rate with 0.4–0.6 mm average particle size of CaSO₄. The 90 g initial weight of CaSO₄ showed a 28.6% higher conversion rate of CH₄ as well as a 21.4% higher conversion for CH₄ with a flow rate of 50 ml/min.

Unsupported mixed metal oxygen carriers such as Fe-Cu and Mn-Ni were tested in a batch fluidized bed reactor by Frick et al. [11] using CH₄, H₂ and CO as fuel gases. Average CO₂ yield from methane was reported to be higher than 85% at 1050 °C for all samples. The activation energies for oxidation and reduction reactions are another key parameter to determine the reactivity of oxygen carriers. Typical values for the activation energy of reduction reaction are found to be less than 100 kJ/mol, and for the oxidation reaction are higher than 100 kJ/mol; however, values of activation energies greater than 300 kJ/mol are considered to be high [2]. Hossain and Lasa [12] evaluated the

activation energy and reaction mechanisms for bimetallic oxygen carriers using O₂-TPO and H₂-TPR. It was found that both reactions were better presented by nucleation and nuclei growth model where the activation energies for oxidation and reduction reactions were found to be 44 kJ/mol and 45 kJ/mol respectively. Jiang et al. [13] tested a bimetallic oxygen carrier (Fe-Cu) for its reactivity in both TGA and batch fluidized bed reactor using H₂ and CO as fuel gases. It was observed that as the Cu content increased (5% to 20%), the redox reactions rates (using H₂) also increased, as well as the agglomeration of Cu particles in the batch fluidized bed reactor. Interpretation of possible reduction reaction mechanisms of bimetallic oxides oxygen carrier (CuO-Fe₂O₃) was reported by Siritwardane et al. [14] who observed that methane fully reduced both bimetallic oxide precursors (CuO-Fe₂O₃/Al₂O₃) to Cu and Fe metals due to the synergetic effect of released oxygen, and dispersion of CuO and Fe₂O₃ on CuFe₂O₄. Bhavsar et al. [15] investigated the phase stability of bimetallic oxygen carriers (Fe-Mn/CeO₂) in both TGA and fixed-bed reactors and reported that a high ratio of ceria-supported Fe to Mn oxygen carrier resulted in de-alloying and re-alloying phenomena that unfavorably enhanced the solid-state diffusion process in the Fe phase.

Kinetic measurements and evaluation for metal-based oxygen carriers have been reported in the literature. However, the literature contains few detailed explanations of the experimental reduction reaction pathways of supported bimetallic (Co, Cu, Ni, Fe) oxygen carriers. Therefore, studies of the intrinsic and global kinetics for methane-fuelled CLC redox reactions of supported bimetallic oxygen carriers are required to have an understanding of reaction mechanism. This paper provides a bridge to link innovative future approaches to efficient performance of bimetallic oxygen carriers and previous studies that showed that the use of some metals with substantially high oxygen carrying capacity were considered expensive and/or toxic to humans and the environment (i.e. Co, Cu, Ni) while others with low oxygen carrying capacity (i.e. Fe) were inexpensive. The aim of this paper is to provide comprehensive studies on the reactivity and kinetics of supported bimetallic oxygen carriers (Ni-Co, Ni-Cu, Ni-Fe), and to interpret the most dominant reduction reaction pathways when methane is used as a fuel. The outcomes of this study will provide valuable information about chemically stable and supported bimetallic oxygen carriers in the methane-fuelled CLC system, which could help in improving precursor conversion level, increasing CO₂ selectivity among other gases such as H₂ and CO, and reducing the precursors-supports interactions.

2. Materials and methods

2.1. Materials

The synthesized oxygen carriers used in this study are as follows: Ni-Co/Al₂O₃, Ni-Co/CeO₂, Ni-Co/TiO₂, Ni-Co/ZrO₂, Ni-Cu/Al₂O₃, Ni-Cu/CeO₂, Ni-Cu/TiO₂, Ni-Cu/ZrO₂, Ni-Fe/Al₂O₃, Ni-Fe/CeO₂, Ni-Fe/TiO₂, Ni-Fe/ZrO₂. They were prepared using the incipient wetness impregnation method. The following nitrates forms of precursor were purchased from Sigma Aldrich Canada: cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O), copper nitrate trihydrate (Cu(NO₃)₂·3H₂O), iron nitrate nonahydrate (Fe(NO₃)₃·9H₂O), and nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O). The support oxide CeO₂ (99.995%) was purchased from Sigma Aldrich Canada, while Al₂O₃ (γ-alumina, 99.9%), TiO₂ (99.5%), and ZrO₂ (99.5%) were purchased from Alfa-Aesar. Both metal nitrates and support oxides were used without any further modifications. A beaker was initially filled with 50 ml of DI water, and then a starting aqueous solution was used where the respective nitrates form of precursor #1 (i.e. Ni) was dissolved for 10 min followed by nitrates form of precursor #2 (i.e. Co, Cu, Fe). The support oxides (Al₂O₃, CeO₂, TiO₂, ZrO₂) were then added to the mixture and stirred for 24 h. The mixture was then heated to 75 °C until all water evaporated. The sample was then collected, and dried in a conventional oven at 120 °C for 12 h to remove all moisture. The sample was then calcined in air at 800 °C for

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