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Full Length Article

Gaseous state oxygen carrier for coal chemical looping process

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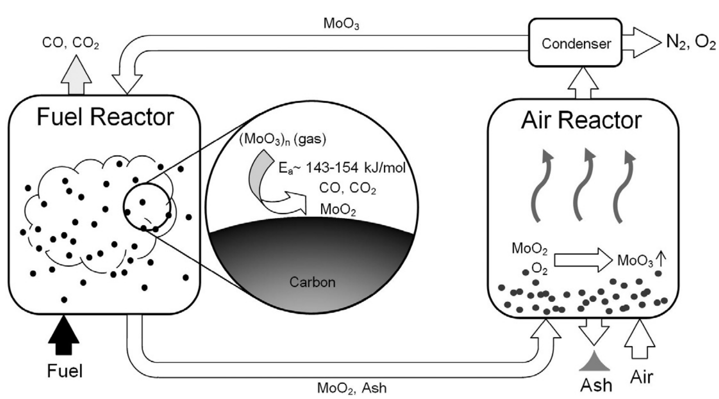
HIGHLIGHTS

- MoO_3 was proposed as a new oxygen carrier for coal chemical looping process.
- This volatile oxygen carrier offers unique advantages over traditional carriers.
- The reaction of gas-phase MoO_3 with carbon was first reported.
- Different operation conditions of fuel reactor were simulated.

GRAPHICAL ABSTRACT



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ABSTRACT

Traditional chemical looping technologies utilize solid oxygen carriers and has some disadvantages, especially when solid fuels like coal are used. In this work, a novel chemical looping process using gaseous metal oxide as oxygen carrier was proposed. The reaction of activated charcoal with gas-phase MoO_3 was studied for the first time. The experiments were conducted isothermally at different temperatures in a fixed-bed reactor. The apparent activation energy of the reaction was calculated and suitable kinetic models were determined. The results and analysis showed that the proposed concept has potential in both coal chemical looping combustion and gasification process.

1. Introduction

The concentration of CO_2 in the atmosphere has dramatically increased in the last few decades, from 320 ppm in the 1960s, to over 400 ppm in 2015 [1]. Since CO_2 is the most important anthropogenic greenhouse gas, the increase in CO_2 concentration is likely linked to global warming and climate changes [1,2]. Meanwhile the consumption of fossil fuels is still rapidly increasing around the world, contributing over two-thirds of global CO_2 emission [1]. A number of CO_2 capture processes has been proposed, including oxyfuel combustion, pre-combustion and post-combustion [3]. Most of these methods have a high cost of operation and a large energy penalty. Chemical looping combustion (CLC) is one of the most promising technologies that can efficiently utilize fossil fuel while capturing CO_2 with a lower energy penalty and thus lowering cost [4–11]. Chemical looping gasification (CLG) is a clean and effective technology for syngas generation from coal [12].

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1.1. Chemical looping systems

Chemical looping combustion typically consists of two interconnected reactors: a fuel reactor and an air reactor. A solid oxygen carrier (usually metal oxides) circulates between the two reactors to carry oxygen from air to fuel.

In the fuel reactor, an oxygen carrier particle transfers its lattice oxygen to fuel that primarily produces CO_2 and steam while being reduced itself. Therefore, the need for additional separation of CO_2 is eliminated. The reduced oxygen carrier is then transported to the air reactor, where it is oxidized by air. The flue gas from the air reactor contains unreacted oxygen and nitrogen and can be released into the atmosphere with minimum environmental impact.

Since the fuel never comes in direct contact with air, CLC has the potential to eliminate the formation of NO_x and capture CO_2 efficiently [13]. CLG shares the principles with CLC. Instead of producing CO_2 and steam in the fuel reactor, CLG supplies inadequate oxygen and generates CO and H_2.

CLC was initially conceived for the combustion of natural gas. There has been an increasing interest in using coal as fuel in CLC, due to its abundance and the increasing demand of coal-powered electricity around the world. However, sluggish kinetics and oxide-ash separation must be addressed during CLC when using a solid fuel such as coal [14,15]. Two approaches are used when CLC is used to burn solid fuel [3]. The first option is to introduce gasification agents such as steam or CO_2 into the fuel reactor. The second option is to use an oxygen carrier that will release gas-phase oxygen in the fuel reactor [16–25]. Nonetheless, the carrier-ash separation and carrier robustness are still significant hurdles.

1.2. Oxygen carriers

One of the most important factors that will affect the performance of a CLC system is the choice of the oxygen carrier. The reactivity, oxygen capacity and recyclability of the oxygen carrier particle are important properties to consider.

A number of studies on oxygen carriers have been performed in the last decade [1,3,4,26]. More than 900 oxygen carrier particles with different metal oxide/support combinations have been tested [13]. The most commonly used oxygen carriers are Fe, Ni, Co, Mn, and Cu. The metal oxides are combined with an inert support material, which provides a higher surface area and increases the mechanical strength [26,27]. Some natural minerals are also used as oxygen carriers, such as ilmenite ($FeTiO_3$), due to their low cost [13].

Development of oxygen carriers with excellent reactivity and stability remains one of the challenges for CLC [3]. Despite the selection of metal and support material, there are inherent issues regarding traditional solid oxygen carriers. Solid oxygen carriers lose their reactivity in limited redox cycles [13,27–36]. In the air reactor, it is necessary to drain the ashes from the system to avoid its accumulation. The solid oxygen carrier particles mixed with ash cannot be completely separated, causing partial loss of the oxygen carrier during the draining process [14,15,28,37–49].

1.3. Novel concept using gaseous oxygen carriers

The authors have conceptualized the "Gaseous Oxide Assisted Looping (GOAL)" [50] combustion technology that would obviate the hurdles of traditional chemical looping (Fig. 1). Here, the oxygen carrier is a metal oxide that is in the vapor phase at the temperature and pressure within the fuel reactor, but the reduced form of the metal oxide is solid under the same conditions. Thus, in the fuel reactor, the metal oxide vapor and the coal react as in a gas–solid reaction, thereby ensuring rapid kinetics. This produces a reduced oxygen carrier that precipitates as a solid onto the ash. The ash-reduced carrier composite is transported to the air reactor where the carrier is re-oxidized. Then the solid materials are heated to produce the metal oxide vapors that are subsequently fed back into the fuel reactor. The simple process of heating completely separates the ash from the metal oxide. In addition to maintaining a gas-solid reaction and simplifying oxide-ash separation, it must be noted that the metal oxide is in its vapor form, i.e. molecular form. As a result, factors that define the useful life of a carrier no longer play a part.

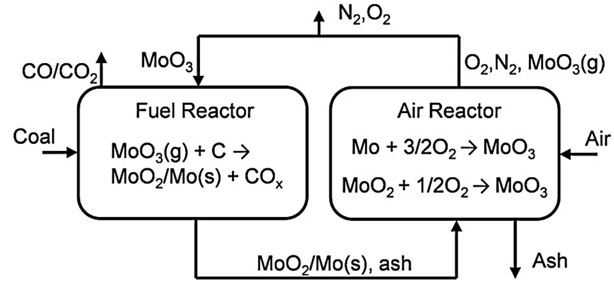

Fig. 1. Schematic of gaseous oxide assisted looping (GOAL) using MoO_3 as oxygen carrier.

Compared to regular CLCs, the key advantages of the proposed system includes:

1. Simplified ash separation. In the air reactor, oxygen carriers separate easily separated from the ash by evaporation.
2. High oxygen carrying capacity. Without the need of supporting materials, the oxygen carrying capacity of the oxygen carrier is increased.
3. Extended lifespan. Traditional oxygen carriers' reactivity decrease over cycles inevitably. A gaseous oxygen carrier can avoid such problem.
4. Fast reaction with solid fuels. In the fuel reactor, the oxidation of fuel is a gas-solid reaction. It has a higher reaction rate and fuel efficiency than a solid-solid reaction.

The choice of oxygen carrier must be in its vapor form under the fuel reactor conditions. Most transition metal oxides used as oxygen carrier, including Fe_2O_3, NiO and CuO, decompose at high temperature. In comparison, MoO_3 and Re_2O_7 molecules can stably exist in the gas phase [51,52]. MoO_3 has a melting point of 801 °C and a boiling point of 1155 °C. Re_2O_7 has a boiling point of 360 °C [53]. In this work, MoO_3 was selected as the oxygen carrier. In the air reactor, MoO_2 or Mo metal is oxidized by air. In the fuel reactor, MoO_3 react with the fuel in its gaseous form. Once out of the air reactor, MoO_3 can separate from O_2 and N_2 by condensation. The use of MoO_3 allows for a higher oxygen carrying capacity. For MoO_3/MoO_2 couple, the oxygen capacity is 11.1% wt. The commonly used oxygen carriers with support material have an oxygen capacity of 1%–9% wt [4].

MoO_3 starts to evaporate when the temperature is above 600 °C. The enthalpy of sublimation of MoO_3 is 337 kJ/mol [54]. Table 1 shows the vapor pressure of MoO_3 at different temperatures.

A number of studies have been conducted on the kinetics of MoO_2 oxidation and evaporation of MoO_3 [57–61]. No research has been conducted on the oxidation of carbon by gaseous MoO_3, but reaction (5) and (6) are thermodynamically favorable [62]. The relevant chemical reactions reported by literatures are listed in Table 2.

To date, there has been no report on using volatile metal oxides as oxygen carriers in CLC or CLG systems. This work investigated the possibility of this concept. The performance of MoO_3 as a gas-phase oxidizer for activated charcoal was reported.