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Full Length Article

Mechanism of lignite-to-pure syngas low temperature chemical looping gasification synergistic in situ S capture

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ABSTRACT

Phosphogypsum (PG) is a by-product produced in phosphate fertilizer industry, and can be used as the oxygen carrier for the process of chemical looping gasification (CLG) of lignite to produce syngas. However, the temperature for this process is around 1173 K, and consumes a lot of energy. Additionally, during the process, a lot of H_2S is yielded, which seriously affects the quality of syngas. Therefore, in order to save energy and improve the quality of syngas, this paper proposes a new oxygen carrier to lower the reaction temperature of the CLG to produce syngas while simultaneously capturing sulfur (S) from the gas product. Meanwhile, thermodynamic calculations and laboratory experiments have been used to investigate the characteristics of proposed Ni/PG material along with the mechanism of the process. The results showed that the Ni element existed in the form of small NiO crystals on the surface of PG while acting as the oxygen carrier, and possessed excellent reactivity and recyclability characteristics. Furthermore, the use of the material can reduce the reaction temperature of the CLG for syngas production and purify syngas through the chemical reaction: $3Ni + 2H_2 S \rightarrow Ni_3S_2 + 2H_2$. During the reduction process, the main reactions for syngas production consisted of solid-solid and gas-solid reactions, and therefore, the Shrinking Core Model (SCM) was the most probable mode of this process. Furthermore, the main chemical reaction for the regeneration of Ni/PG was a gas-solid reaction.

1. Introduction

Chemical looping gasification (CLG) is based on chemical looping process technology [1,2]. In this technology, the solid fuel is physically mixed with the oxygen carrier in a fuel reactor, where the oxygen carrier reacts with volatiles and produces gas products containing high concentrations of hydrogen (H_2) and carbon monoxide (CO) due to the gasification of char [3]. Compared with the chemical looping combustion, CLG along with the partial oxidation can produce syngas (consisting mainly of CO, H_2 and some CH_4) [4]. Additionally, in this process, steam or CO_2 could be added to the fuel reactor to encourage steam and CO_2 reforming [4–8].

Syngas has been widely used as the raw material for producing various chemicals, such as synthesis of gasoline, diesel, methanol, synthetic ammonia and coal gas mainly containing carbon monoxide and hydrogen [5–10]. Syngas can be produced using either coal or coke gasification and may also come from light hydrocarbons, natural gas, naphtha and heavy oil [10,11]. Based on initial calculations, it is suggested that the CLG process for syngas production has the potential to obtain higher power efficiency and lower costs than other evaluated technologies [3,12]. The CLG process exhibited a net higher efficiency for the production of syngas than other syngas production processes [3,13,14]. The inorganic species present in ash acts as an effective gasification catalyst, and makes CLG of biomass superior to that of the coal [4,15]. Lignite belongs to low-rank coal and has high moisture, volatile matter, low calorific value, and high-sulfur, all of which seriously influence its uninterrupted use [16–20]. Besides, Yunnan (China) has abundant lignite resources. In the current work, lignite was used as the solid fuel. Therefore, some of the sulfur element in lignite can be released during the CLG process, which is bad for the quality of syngas. Therefore, it is important to find a way to purify syngas produced from the CLG of lignite.

A key issue for the CLG technology is the selection of an oxygen carrier that has suitable properties [21–32]. These properties include: (1) capability to transport sufficient oxygen; (2) high reactivity for reduction and oxidation reactions, and maximum fuel conversion; (3) low cost, which is a decisive factor for large scale industrial applications; and (4) low toxicity and environmentally-friendly characteristics. While selecting a suitable oxygen carrier, all these characteristics should be considered and efforts should be made to strike a balance among them.

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Nomenclature

syn	molar of syngas generation (mol)
Xc	carbon of lignite conversion (%)
f_i	carbonaceous gases composition
n_i	molar of carbonaceous gases
i	i could be CO, CH_4 and H_2
f_{CH_4}	composition of CH_4 (%)
f_{co}	composition of CO (%)
f_{CO_2}	composition of CO_2 (%)
n_{CH_4}	molar of CH_4 (mol)
n_{co}	molar of CO (mol)
n_{CO_2}	molar of CO_2 (mol)
ΔG	Gibbs free energy
ΔG^θ	Gibbs free energy at the same temperature under standard pressure.
R	Gas constant
Q	Reaction entropy

Abbreviations

PG	phosphogypsum
Ni/PG	compound oxygen carrier of Ni and phosphogypsum
CLG	chemical looping gasification
XRD	X-ray diffraction
BET	Brunner-Emmet-Teller measurements
TGA	Thermogravimetric analyzer
SEM	Scanning Electron Microscope
CGSM	Changing Grain Size Model
SCM	Shrinking Core Model

In many previous studies, single metal oxides, combined or mixed metal oxides, and inert supports were extensively investigated as potential oxygen carriers in CLG due to their high reactivity and environmentally friendly nature [23,24]. However, there are several inherent disadvantages in them, such as slow oxygen-carrying rate of Fe-based oxygen carriers [25], and low melting point and agglomeration of Cu-based oxygen carriers [26]. Comparatively, $CaSO_4$, and sulfide, which possess high oxygen carrying capacity, have garnered a lot of attention [27–29]. For example, $CaSO_4$ is the favored industrial scale oxide [30–32], and has outstanding oxygen storage and oxygen releasing capabilities, which it achieves through the circular switch of $CaSO_4$/CaS redox couple. Additionally, it has been applied for syngas production as an important oxygen carrier in CLG technology due to its low toxicity and environmentally friendly nature [10]. Compared with the synthetic materials, the natural minerals and waste residues gradually gained attention of researchers [3]. Furthermore, waste residues have been used as the sources of oxygen. Phosphogypsum (PG) is a by-product of wet phosphoric acid [33–35], and has become the primary barrier for the development of phosphate fertilizer industry due to its low utilization rate, large-tonnage output, and environmental harm [33–37]. However, $CaSO_4$ is the main component of PG, which owns outstanding oxygen storage and oxygen releasing characteristics. Additionally, calcium sulfate has favorable thermal properties and high syngas selectivity [10,38]. It is also worth noticing that CaS is the major product during the reduction of PG, which can be easily oxidized back to $CaSO_4$. After several circulations of PG, it still shows great stability [39]. Additionally, when the size of PG was less than 0.3 mm, the decomposition product of PG-CaS showed great stability without any sintering phenomenon [40–43]. Therefore, PG can be one of the most suitable oxygen carriers for CLG technology. It is not only beneficial to the environment, but can also turn "waste“ into "treasure”, thus making it a milestone for social sustainable development and circular economy.

In a previous study, PG was applied as the oxygen carrier for syngas production in CLG of lignite. However, the reduction temperature was around 1173 K, which required a lot of energy. In large-scale industrial production, energy consumption is the most important factor that determines whether the process scheme can be implemented or not. Additionally, the energy consumption of chemical reaction constitutes a large part of total energy required. Higher the temperature of the reaction, more is the energy needed. In order to deal with this problem, a suitable oxygen carrier is needed. It is well known that a suitable compound oxygen carrier may provide better properties than those of the individual single oxygen carriers [3]. For example, the compound oxygen carrier of $Cu_{0.95}Fe_{1.05}AlO_4$ could deal with the spinel structure of Cu and Fe [44]. Similarly, Fe_2O_3-MnO_2 supported on ZrO_2 showed a better reaction performance and thermal stability for chemical looping process [45]. Besides, several inert compounds have been tested as supporting materials for the preparation of particles of Mn-based oxygen carrier to improve its performance [3]. In addition, Jin et al. improved the reactivity of Co-based oxygen-carriers by impregnating several supports [46]. A suitable compound oxygen carrier can also reduce the high reaction temperature of CLG. For example, to reduce the PG decomposition temperature, Yan et al. added Fe element to PG using impregnation method, which significantly reduced the decomposition temperature of PG [47]. Therefore, PG based compound oxygen carriers might deal with the high temperature problem of the CLG process to produce syngas. Ni-based oxygen-carriers have shown very high reactivity and good performance for chemical looping technique [3]. Additionally, other important characteristics of the Ni-based materials are their favorable qualities with regards to sulfur present in the fuel [48–50]. The deactivation of an oxygen carrier due to the presence of H_2S in the fuel gas has often been observed [48]. The use of an impregnated Ni-based oxygen-carrier in a 500 W_{th} unit always resulted in the formation of nickel sulfide when H_2S was present in the fuel gas [50]. Therefore, the Ni and PG compound oxygen carriers, which might capture H_2S to purify the syngas and reduce the reaction temperature, are important in improving the overall efficiency of the CLG process.

In order to save energy and get more pure syngas, a Ni and PG based compound oxygen carrier was prepared (herein, called the Ni/PG). The reactivity and recyclability results of the Ni/PG were studied through laboratory experiments. Furthermore, experiments have been conducted in conjunction with thermodynamics calculations to analyze the ability of Ni/PG to reduce the reaction temperature and capture H_2S during the production of syngas. To better understand this process, the reaction mechanism of lignite's CLG using Ni/PG has been researched.

2. Experimental

2.1. Sample preparation

The catalysts were prepared using a precipitation method. Firstly, a specified amount of nickel (II) nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$) was dissolved in deionized water under vigorous stirring at 338 K for 20 min. The support (powdered PG) was slowly added to the nickel nitrate aqueous solution to form a mixture. Next, the mixture was stirred for 120 min at 338 K, while ammonia was used to adjust the pH of the solution from neutral to slightly alkaline (8–9). Finally, the obtained samples were dried overnight at 393 K in an oven, and then, calcined at 773 K for 300 min in a muffle furnace to obtain the catalysts. The obtained compound oxygen carrier was labelled as Ni/PG. The molar ratio of Ni to PG was varied between 0.25 and 1.5, and based upon the ratio, the samples were named as 0.25Ni/PG, 0.5Ni/PG, 1.0Ni/PG, 1.25Ni/PG and 1.5Ni/PG. Additionally, the surface