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Activation of ilmenite as an oxygen carrier for solid-fueled chemical looping combustion

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HIGHLIGHTS

- Improving ilmenite OC's performance by adding a small amount of foreign elements.
- Gasification and combustion efficiency are correlated to OC reactivity and selectivity.
- Strong catalyzed *WGSR* from K-added OCs play vital role in improving gasification.
- Cu-coating hinders Fe-element segregation on the ilmenite surface during redox cycle.
- Ca-, Ni- and Mn-added ilmenite OCs did not show promising prospects.

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ABSTRACT

Ilmenite ore is one of the promising oxygen carriers (OCs) used for coal-fueled Chemical-Looping Combustion (CLC) for electricity generation and CO_2 capture. However, the low reactivity and natural activation of ilmenite OC are two major constrains impeding its application. This effort is to improve ilmenite OC's performance by introducing a small amount of foreign elements, including alkali or alkaline earth metals (K and Ca) and transition metals (Cu, Mn, and Ni). Coating and re-granulation methods were used to prepare OCs where ilmenite ore was the primary constituent. The reactivity, transport capacity, and selectivity of these ilmenite-based OCs with wet syngas, as well as their performances in coal char-fueled CLC were investigated using a TGA, fixed- and fluidized-bed reactors. The addition of K-element significantly improved the OC's reactivity with wet syngas and coal char. The strong catalytic function for *WGSR* from K-added OCs was found to play a vital role. Cu-coating hindered effectively Fe-element segregation on the surface of ilmenite OC during cyclic reaction, and the OC structural integrity was well maintained. Ca-, Ni- and Mn-added ilmenite OCs did not show promising prospects. The gasification rate and combustion efficiency could be respectively correlated to the reactivity and selectivity of different OCs except for the K-added samples.

1. Introduction

Due to the impact of CO_2 emissions on climate change, reducing CO_2 production from fossil fuel combustion, including coal combustion is an agent need. The novel process of coal-fueled CLC with iron-based OCs has been extensively studied for simultaneous electricity generation and CO_2 capture [1,2]. Compared to post-combustion technologies, the coal-fueled CLC technology possesses much lower energy penalties for CO_2 capture by avoiding costly gas separation processes. The plant efficiency of the coal-fueled CLC is approximately 36% with ambient pressure [3] and as high as 42–43% with the pressurized combined cycle [4]. The key to successful CLC process is to develop an optimal OC material. The following OC criteria are needed [1,5]

- High reactivity with fuel and oxygen.
- High fuel conversion to CO_2 and H_2O, or high selectivity for high purity CO_2 stream.
- High oxygen transport capacity to minimize solid circulation.
- Chemical and mechanical stability during successive redox cycles.
- High resistance to attrition if a fluidized bed reactor is used.

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Nomenclature

d_{50}	median diameter (μm)
f_i	volumetric fraction of *i* gas component
J	quotient of *WGSR* reaction
K_{eq}	equilibrium constant of *WGSR*
m	mass of OC during reduction (g)
$m_c(t)$	total mass of carbon in fuel char converted to gas at time of *t* (g)
m_{ox}	mass of OC in the full oxidized form (g)
m_{total}	total mass of carbon introduced to the reactor (g)
m_{red}	mass of OC in the reduced form obtained under experimental condition (g)
P_i	integral partial pressure of syngas component *i*
r_{OC}	mass-based conversion of OC per unit time
$\bar{r}_c$	average carbon conversion rate
S_{syn}	instantaneous selectivity during OC reduction
$\bar{S}_{syn}$	average of OC's instantaneous selectivity
t	time (min)
T	temperature (K)
X_{OC}	mass-based conversion of oxygen carriers

Greek letters

η_{syn}	combustion efficiency of intermediate syngas in the solid-fueled CLC
$\bar{\eta}_{syn}$	average combustion efficiency
$\triangle X'_{OC}$	the amount of oxygen transferred to fuels/total mass of OC

Acronyms

AR	air reactor
CFB	circulating fluidized bed
CLC	chemical looping combustion
FR	fuel reactor
FG	freeze granulation
OC	oxygen carrier
TGA	thermogravimetric analyzer
WGSR	*water-gas-shift* reaction
XRD	X-ray diffraction
XRF	X-ray fluorescence

- No carbon deposition to avoid release carbon as CO_2 in the air reactor (AR).
- Environmentally safe and non-hazardous.

These properties above should remain in long term operation. For the solid-fueled CLC, OCs should also be highly ash-resistant because they are directly mixed with coal ash in the fuel reactor (FR). Otherwise, agglomeration and reactivity decay are unavoidable. In order to avoid coal ash accumulation in the system, separating coal ash from the bio-mixtures is needed, but this will lead to appreciable loss of OCs with coal ash stream. Thus, low-cost iron-based OC materials, especially solid waste and natural materials are more favorable for the combustion of solid fuel [6]. A significant improvement in gasification rate in the FR can be realized by using proper OCs [7]. The presence of OC rapidly lowers the fraction of intermediate syngas, CO and H_2, both of which are gasification inhibitors [8]. High reactive with syngas components is one of the most important properties of an OC desired for the solid-fueled CLC.

Among iron-based OCs, ilmenite ore is a suitable material for coal-fueled CLC [9]. Ilmenite ore, naturally in a reduced form, is primarily composed of $FeTiO_3$. Its full oxidized form contains Fe_2TiO_5, TiO_2 and a small amount of Fe_2O_3. When it is used as OCs, Fe_2TiO_5 and Fe_2O_3 are the active phases. Ilmenite has been investigated as one of the most promising OC material for the future commercial application [9–12]. Compared to other iron-based OCs, ilmenite possesses high oxygen transport capacity. The major component of ilmenite, Fe_2TiO_5, is reduced to $FeTiO_3$ in CLC process [9], resulting in a lattice oxygen transport capacity of 5.0 wt.%. Both Fe_2TiO_5 and Fe_2O_3 in ilmenite OC have favorable thermodynamics to convert syngas to CO and H_2O. The equilibrium constants of the two redox systems ($Fe_2TiO_5/FeTiO_3$ and Fe_2O_3/Fe_3O_4) are higher than 10^3, suggesting almost complete fuel conversion [1]. High conversion and reactivity of ilmenite ore OCs with syngas were also confirmed experimentally [13]. The oxidation of the reduced ilmenite is a fast reaction, and during multi-redox cycle, complete re-oxidation of each cycle could be reached [9]. The performance of ilmenite OCs used for coal–fueled CLC had been tested in a batch fluidized bed reactor and the influences of gasification agent and temperature were investigated [14]. An ilmenite OC was first tested in continuous mode in a 10 kW_{th} CLC unit using coal and petro-coke as fuel at Chalmers University of Technology [15,16]. The results from these studies showed favorable OC fluidization properties and high agglomeration resistance. Technische University Darmstadt (Germany) successfully demonstrated an auto-thermal operation of a 1 MW_{th} CLC unit using ilmenite OC and hard coal [17] despite the low conversion of intermediate syngas and solid char in the FR. A detailed engineering design of coal-fueled CLC boiler was performed at a commercial scale (1000 MW_{th}), where ilmenite ore was selected as the OCs to investigate the mass and heat balance, gas-solid flow, solid inventory, combustor configuration, and the cost of boiler [18].

The reaction rate of ilmenite OC with either CO or H_2 is high, but ilmenite's ability to enhance gasification in CLC has been reported as lower relative to other active OCs, such as iron- and manganese-ores [19,7]. The in-situ gasification rate of CLC with ilmenite OCs is about 30% higher than the external gasification [14]. Because relatively low temperature is adopted in CLC process where the gasification reaction is chemically controlled, the improved gasification due to the use of ilmenite OC would not likely lead to a significant difference. With slow gasification, a certain amount of unconverted coal char would slip into the AR with the OC stream, significantly lowering the carbon capture efficiency. Therefore, improving the reactivity of ilmenite with solid fuel is necessary. The natural activation of ilmenite in successive redox cycles, as it can be found when using both gaseous and solid fuels [20,12], may cause negative impact. Natural-activation slightly increases OC reactivity but decreases the oxygen transport capacity because more Fe_2O_3 phase is created from the decomposition of Fe_2TiO_5. The natural - activation process is accompanied by the gradual formation of an external Fe_2O_3-rich layer, which leads to easier particle rounding and detachment of the external layer. Because of these disadvantages, the lifetime of ilmenite OC is estimated at 1700 h for the operation of CFB reactor [21].

Not much research has focus on improving the performance of ilmenite OCs for the gas-fueled CLC process. A physical mixed oxide of ilmenite and NiO_2-based OC was reported to outperform ilmenite for CH_4 combustion [5]. Metallic Ni is believed to catalyze the decomposition of CH_4 into reactive intermediates, CO and H_2.