Activation of Ilmenite as an Oxygen Carrier for Solid-fueled Chemical Looping Combustion

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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 CO₂ capture. However, the low reactivity and natural activation of ilmenite OC are two major constraints 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 WGS 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.

Key words: Chemical looping combustion; Iron-based oxygen carrier; Ilmenite; Solid fuel

1. Introduction

Due to the impact of CO₂ emissions on climate change, reducing CO₂ 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 CO₂ capture [1, 2]. Compared to post-combustion technologies, the coal-fueled CLC technology possesses much lower energy penalties for CO₂ 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 CO₂ and H₂O, or high selectivity for high purity CO₂ 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
- No carbon deposition to avoid release carbon as CO₂ 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 H₂, 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.

Nomenclature			
d_{50}	median diameter (μm)	<i>Greek Letters</i>	
f_i	volumetric fraction of i gas component	η_{syn}	combustion efficiency of intermediate syngas in the solid-fueled CLC
J	quotient of WGS reaction	$\bar{\eta}_{\text{syn}}$	average combustion efficiency
K_{eq}	equilibrium constant of WGS	ΔX_{OC}	the amount of oxygen transferred to fuels/total mass of OC
m	mass of OC during reduction (g)	<i>Acronyms</i>	
$m_c(t)$	total mass of carbon in fuel char converted to gas at time of t (g)	AR	Air Reactor
m_{ox}	mass of OC in the full oxidized form (g)	CFB	Circulating Fluidized Bed
m_{total}	total mass of carbon introduced to the reactor (g)	CLC	Chemical Looping Combustion
m_{red}	mass of OC in the reduced form obtained under experimental condition (g)		
P_i	integral partial pressure of syngas component i	FR	Fuel Reactor
r_{OC}	mass-based conversion of OC per unit time	FG	Freeze Granulation
$\bar{r}_c$	average carbon conversion rate	OC	Oxygen Carrier
S_{syn}	instantaneous selectivity during OC reduction	TGA	Thermogravimetric Analyzer
$\bar{S}_{\text{syn}}$	average of OC's instantaneous selectivity	WGS	Water-Gas-Shift Reaction
t	time (min)	XRD	X-ray Diffraction
T	temperature (K)	XRF	X-ray fluorescence
X_{OC}	Mass-based conversion of oxygen carriers		

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 FeTiO₃. Its full oxidized form contains Fe₂TiO₅, TiO₂ and a small amount of Fe₂O₃. When it is used as OCs, Fe₂TiO₅ and Fe₂O₃ 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, Fe₂TiO₅, is reduced to FeTiO₃ in CLC process [9], resulting in a lattice oxygen transport capacity of 5.0 wt.%. Both Fe₂TiO₅ and Fe₂O₃ in ilmenite OC have favorable thermodynamics to convert syngas to CO and H₂O. The equilibrium constants of the two redox systems (Fe₂TiO₅/FeTiO₃ and Fe₂O₃/Fe₃O₄) are higher than 10³, 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 (1,000 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 H₂ 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 Fe₂O₃ phase is created from the decomposition of Fe₂TiO₅. The natural -activation process is accompanied by the gradual formation of an external Fe₂O₃-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 1,700 hours 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 NiO₂-based OC was reported to outperform ilmenite for CH₄ combustion [5]. Metallic Ni is believed to catalyze the decomposition of CH₄ into reactive intermediates, CO and H₂. Bao et al. found that the reduction reactivity of ilmenite OC impregnated with 15 wt % K⁺ was 8 times faster than that of the raw ilmenite when CO was used as fuel [22].

The focus of this study is to improve the performance of ilmenite OCs for the solid-fueled CLC by introducing a small amount of foreign elements to OC particles. Re-granulation and coating methods were used to prepare the ilmenite-based OCs. The elements used are categorized into two groups: 1.) Alkali or alkaline earth metals (K and Ca) and 2.) Transition metals (Cu, Mn and Ni). It is believed that the addition of alien elements may alter the OC's performance by changing the pathway of OC reduction, altering the lattice oxygen transfer, or by forming a new crystalline phase that is more reducible. The experiments performed focusing on reactivity, oxygen transport capacity, and selectivity of converting wet syngas, and the OCs' performances in coal char-fueled CLC. This work also tentatively reveals the mechanism for the improved OC performance.

2. Experimental

2.1 Materials

Before the preparation of various ilmenite-based OCs, raw ilmenite ore (125-355 μm) was stabilized in air at 950 °C for 24 hours. The ilmenite (200.0 g for each batch) was then activated by 5 redox cycles in a fixed reactor. A gas stream containing 2.0 NL/min CO, 1.5 g /min steam, and 2.0 NL/min N₂ was used in 10-minute reduction at 950 °C, while 10 vol.% O₂ was introduced during regeneration. The chemical

composition of the activated ilmenite in its fully oxidized form is 52.87% Fe₂O₃, 33.8% TiO₂, 5.7% SiO₂, 3.6% Al₂O₃, 2.8% MgO and 0.9% CaO.

The activated ilmenite (125-355 µm) and its crushed powder (d_{50} =19.5 µm) were the main components used to prepare the OCs by coating and freeze granulation (FG) methods, respectively. The foreign elements, including K, Ca, Cu, Mn and Ni, were added to ilmenite in their nitrates, which were converted to oxides during calcination. In the FG method, 200.0 g of fine powder, the desired amount of nitrates, 330.0 g deionized water, and 50.0 g polyvinyl alcohol (Sigma-Aldrich, St. Louis, MO) was mixed to make into homogenous slurry. The slurry was then sprayed into liquid nitrogen to form frozen spherical particles, which were subsequently dried in a vacuum freeze dryer. Finally, calcination was performed at high temperature to stabilize the foreign elements and to provide sufficient mechanical strength. In the coating method, 200.0 g of activated ilmenite was poured into the prepared solutions (100.0 g deionized water and the desired amount of nitrates), stirred for 24 hours, and dried at 95 °C. The dry samples were then calcinated at 950 °C for 6 hours. The activated ilmenite and FG samples without the addition of foreign element were used as references. The particle size of the OCs used for experimentation was 125 to 355 µm. Their designations and properties are listed in [Table 1](#).

Coal char (d =180-355 µm), prepared from Power River Basin coal, was used as fuel. During preparation, the parent coal was heated in a fixed bed reactor at 800 °C for 20 min. 3.0 NL/min of N₂ flow was used to carry the gas products out of the reactor during pyrolysis. The proximate and ultimate analyses and ash analysis of PRB coal char are presented in [Table 2](#) and [Table 3](#). Here the ash sample was obtained from steam-char gasification at 950 °C, and its composition was determined with XRF analysis.

Table 1 Ilmenite-based oxygen carriers

Sample	Fraction of alien elements*	Calcination Temperature	BET Surface Area	Crushing Strength	XRD Analysis (oxidized form)
	Wt. %	°C	m ² /g	N	
Activated-I	-	950	0.28	4.5	Fe ₂ TiO ₅ , TiO ₂
- Used			0.40	3.7	Fe ₂ TiO ₅ , Fe ₂ O ₃ , SiO ₂
FG-I	-	1100	0.46	2.5	Fe ₂ TiO ₅
SK ₂ O(5)-I	5.0	950	0.24	4.7	Fe ₂ TiO ₅ , Fe ₂ O ₃ , K ₂ (Ti ₈ O ₁₇), K _{1.46} Ti _{7.2} Fe _{0.8} O ₁₆
- Used			0.26	3.2	Fe ₂ TiO ₅ , Fe ₂ O ₃ , K _{1.46} Ti _{7.2} Fe _{0.8} O ₁₆
FG-I- K ₂ O(5)	5.0	1100	0.44	2.3	Fe ₂ TiO ₅ , Fe ₂ O ₃ , K _{1.46} Ti _{7.2} Fe _{0.8} O ₁₆
- Used			0.22	2.1	Fe ₂ TiO ₅ , Fe ₂ O ₃ , K _{1.46} Ti _{7.2} Fe _{0.8} O ₁₆
FG-I-CaO(5)	5.0	1200	0.25	2.6	Fe ₂ TiO ₅ , Fe ₂ O ₃ , CaO, Ca(Ti _{0.8} Fe _{0.2})O _{2.9}
SCuO(5)-I	5.0	950	0.11	4.5	Fe ₂ TiO ₅ , Fe ₂ O ₃ , SiO ₂ , Cu ₃ TiO ₄
- Used			0.15	4.4	Fe ₂ TiO ₅ , Fe ₂ O ₃ , SiO ₂
FG-I-CuO(5)	5.0	1100	0.32	2.4	Fe ₂ TiO ₅ , Fe ₂ O ₃ , TiO ₂
SMn ₃ O ₄ (7.5)-I	7.5	950	0.14	4.3	Fe ₃ Ti ₃ O ₁₀ , Fe ₂ O ₃ , MnO ₂ , Mn ₂ O ₃
FG-I-Mn ₃ O ₄ (7.5)	7.5	1150	0.21	2.3	Fe ₃ Ti ₃ O ₁₀ , Fe ₂ O ₃ , MnO ₂ , Mn ₂ O ₃
SNiO ₂ (2.5)-I	2.5	950	0.22	4.4	Fe ₂ TiO ₅ , Fe ₂ O ₃ , NiO ₂ , Fe ₃ Ti ₃ O ₁₀ , NiTiO ₃
FG-I-NiO ₂ (2.5)	2.5	1150	0.39	2.2	Fe ₂ TiO ₅ , Fe ₂ O ₃ , NiO ₂ , NiTiO ₃

Note: 1. *fully oxidized; 2. FG-freeze granulation, S- coating; 3. I- ilmenite; 4. Used- used after 20 redox cycle

Table 2 Proximate and ultimate analyses of PRB char

Heating Value [MJ/kg]	Proximate Analysis [wt.%]			Ultimate Analysis [wt.%]				
	Ash	Volatiles	Fixed carbon	C	H	O	N	S
27.6	16.28	3.13	80.59	77.4	1.38	1.52	1.72	1.70

Table 3 Ash analysis of PRB char [wt.%]

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	TiO ₂	SO ₃
47.31	17.57	6.1	15.28	4.16	1.0	0.85	1.39	0.96	6.15

2.2 Experiments and procedure

A three-step strategy was implemented in this study. First, the reactivity and selectivity of ilmenite-based OCs were investigated with wet syngas (a mixture of CO and steam). Second, in-situ gasification and intermediate syngas conversion in the coal-char fueled CLC were evaluated in a fluidized bed reactor. Third, the stability and integrity of the best OCs were evaluated in cyclic CLC experiments, which demonstrate the materials' overall performance in the presence of fluidization flow, chemical reaction, and coal ash during long term operation. All experiments were performed at 950 °C.

The reactivity of OCs in wet syngas was investigated in a TGA apparatus equipped with a steam generator (TGA, Netzsch STA 449 F3 Jupiter). 50-60 mg of fully oxidized sample was placed in the crucible and heated to the desired temperature in Ar. Then reduction was performed with a feed stream of 20 ml/min CO, 0.03 g/min steam, and 140 ml/min Ar (corresponding to 10% CO and 20% steam before the furnace). The flow rate of wet syngas was examined at which the external mass transfer limited reaction was avoided.

The OC selectivity was determined using a fixed-bed reactor with wet syngas at conditions of an ideal gas-solid contact. So the results revealed to what extent the wet syngas can be oxidized at different OC conversion. The schematic diagram and description of the fixed-bed facility can be found elsewhere [24]. This facility was also used in fluidized-bed mode for the coal char-fueled CLC experiments. During the fixed-bed experiments, the reducing gas was introduced at the top of reactor, while the resulting gas exited the bottom. The exit gas of the reactor was forced to pass through a cyclone, high temperature filter, cooler, and moisture trap in sequence to remove fine particles and condensate. The gas concentration profiles of O₂, CH₄, CO, CO₂, and H₂ were analyzed by a multi-gas analyzer (Rosemount, X-stream). The reducing gas flow, containing 1.5 NL/min CO, 1.1 g/min steam, and 1.5 NL/min N₂, was fed continuously until the concentrations of unconverted fuel gas in exit stream increased rapidly. The OC loading for each test was 300.0 g, which formed a packed bed > 150 mm.

In the coal char-fueled CLC experiments, 150.0 g OC was loaded, fluidized with N₂ and then heated to 950 °C. Gasification agent (1.5 g/min steam carried by 2.0 NL/min N₂) was introduced to the reactor when the temperature stabilized. Five minutes later, 1.0 g coal char was fed into the hot bed material to start the reduction.

The stability and integrity of the selected OCs were determined by a 20-cycle CLC experiments. The reduction of each cycle followed the same procedure described above. The reduced OC samples were then fully re-oxidized with 10% O₂. Between the oxidation and reduction periods, the reactor was purged with 4.0 NL/min N₂ flow. After 20 cycles, the used OCs were cooled to ambient temperature for sampling and characterization.

2.3 Data evaluation

The behavior of OC reduction was analyzed by the mass-based conversion (X_{OC}) from TGA. The oxygen transport capacity (ΔX_{OC}) is the maximum percentage of mass loss due to oxygen transfer under experimental conditions. They are calculated by

$$X_{OC} = \frac{m}{m_{ox}} \quad (1)$$

$$\Delta X_{OC} = \frac{m_{ox} - m_{red}}{m_{ox}} \quad (2)$$

Where m is the mass of the OC during reduction, m_{ox} is the mass in its full oxidized form, and m_{red} is the mass of the reduced form obtained under experimental conditions. The oxygen transfer rate, r_{OC} is defined as the mass-based conversion per unit time ($r_{OC} = dX_{OC}/dt$, %/min).

The instantaneous rate of carbon conversion is used to evaluate the in-situ gasification in CLC, given by

$$r_c = \frac{dX_c / dt}{1 - X_c} \quad (3)$$

Where X_c is the carbon conversion calculated by

$$X_c = \frac{m_c(t)}{m_{total}} \quad (4)$$

Where m_{total} is the total mass of carbon introduced to the reactor, $m_c(t)$ is the total mass of carbon in fuel char converted to gas at time of t .

From the gas product distribution of the fixed bed reactor, it is possible to calculate the instantaneous syngas conversion rate and OC conversion. The instantaneous selectivity is used [11]

$$S_{syn} = 1 - \frac{0.5f_{CO} + 0.5f_{H_2}}{f_{CO_2} + 0.5f_{CO} + 0.5f_{H_2}} \quad (5)$$

Here f_i is the volumetric fraction of i gas component. Eq. (5) is also applied to calculate the combustion efficiency of intermediate syngas in the solid-fueled CLC, η_{syn} .

The OCs, or its reduced form, may catalyze the WGS in the FR, and influence the final flue gas composition. The OCs' catalytic function for the WGS is evaluated via the quotient of reaction, J , to describe the extent of this reaction as it approaches equilibrium under experimental conditions.

$$J = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} \quad (6)$$

Where P_i is the integral partial pressure of syngas component at the outlet of the reactor (before steam removal). It is calculated by the integrating the mole flow rate of gas component over the reduction period.

3. Results and discussion

3.1 Oxygen transport of OCs with steam in the syngas

The oxygen transport behavior of OCs plays an important role in the improvement of in-situ gasification of CLC. Fig. 1 (a)-(d) shows the value of X_{OC} when the ilmenite-based OCs were reduced with wet syngas in the TGA apparatus. The results of Activated-I reduction with dry gas fuel (20 ml/min CO or H_2 in 180 ml/min Ar) are shown to illustrate the effect of steam in the fuel gas. In the FR, steam is the essential component bathing OC particles. However, the presence of steam reduced the oxygen transport capacity of Activated-I from 16 wt.% (for dry fuels) to 3.4 wt.%. The reduction was significantly slowed

by the reverse oxidation of the reduced OC with steam. Based on these results, wet syngas was used in this study to evaluate the oxygen transport behaviors for all OCs.

The oxygen transport of the FG-I was significantly lower than Activated-I, implying that this OC suffered a great structural change due to granulation. Because both OC's have the same chemical composition, the values of ΔX_{OC} were very close to one another. Different from the Activated-I and FG-I, the reduction of two K-added ilmenite OCs was composed of a fast oxygen transfer stage followed by a second slow stage. The fast stage accounted for about 85% and 80% of ΔX_{OC} for SK₂O(5)-I and FG-I-K₂O(5), respectively. The coating of K appears to reduce the resistance of lattice oxygen transfer on the particle surface. Therefore, the reduction rate of SK₂O(5)-I in the fast stage was higher than Activated-I. The addition of K to the interior of the FG OC appears to improve the transfer rate of lattice oxygen from the interior to the surface. In the fast oxygen transfer stage of FG-I-K₂O(5) ($X_{OC} > 97.2\%$), the value of r_{OC} was 3.0 times higher than the FG-I. Because granulation is detrimental to the reaction, the enhanced rate of oxygen transfer for FG-I-K₂O(5) does not originate from granulation but from the addition of K. The addition of Ca led to very similar oxygen transfer behavior as the FG-I in the first 90 min, but reduced the oxygen transport capacity.

Fig. 1 X_{OC} of different ilmenite-based OCs obtained with TGA

Oxygen transport behaviors of these OCs with the addition of Cu, Mn, and Ni, are presented in Fig. 2(b)-(d). The addition of Cu enhanced the oxygen transport rate and capacity, while the addition of Mn and Ni had little effect on the final transport capacity. $\text{SNiO}_2(2.5)\text{-I}$ showed a similar reduction behavior to Activated-I, while the other OCs with Mn and Ni showed lower oxygen transfer rate than Activated-I. $\text{SCuO}(5)\text{-I}$ performed best among the transition-metal-added OCs. However, the degrees of reduction of the ilmenite ore in $\text{SCuO}(5)\text{-I}$ was not increased as compare to Activated-I. If $\text{SCuO}(5)\text{-I}$ is considered as a physical mixture, containing 95% ilmenite and 5% CuO , the theoretical value of ΔX_{OC} in the wet syngas is 4.23%, which very close to the experimental data ($\Delta X_{\text{OC}}=4.14\%$ for $\text{SCuO}(5)\text{-I}$). The oxygen uncoupling effect (CLOU) [24] was not seen during the heating of $\text{SCuO}(5)\text{-I}$ in the TGA experiments. During the two stage-reductions, the fast reduction stage (the first 55 min) accounted for 97% of ΔX_{OC} . The small amount of highly reducible Cu-Ti-O compounds (Cu_3TiO_4) in the OCs [25-26] is not enough to explain the significant increase of reduction rate. Because the oxidation of Cu_2O or Cu with steam is not spontaneous at high temperature [27], Cu-element on the surface of particles significantly lowers the reverse oxidation of the reduced OC by steam, which led to a higher reduction rate compared to Activated-I OC.

3.2 Selectivity of OCs in converting syngas to CO_2 and H_2O

A preferable OC is expected to retain an adequate ability to convert syngas to CO_2 or H_2O across a wide range of oxygen loss ratio ($\Delta X_{\text{OC}}'$, the amount of oxygen transferred to fuels/total mass of OC). The OC selectivity obtained in the fixed bed reactor is presented in Fig. 2. Because of the thermodynamics and channel flow, the value of S_{syn} was always lower than 1.0. For Activated-I, 0.98 of S_{syn} was achieved until $\Delta X_{\text{OC}}'$ was higher than 0.04. This value was approximate to the thermodynamics (0.995 at 950 °C) when Fe_2TiO_5 in Activated-I is reduced to FeTiO_3 [9]. According to the chemical composition analysis, Activated-I consisted reasonably of 79.3 wt.% Fe_2TiO_5 , 7.37 wt.% TiO_2 , and 13.33 wt.% inert materials (including SiO_2 , Al_2O_3 , and MgO). Therefore, the reduction of Activated-I would lead to oxygen loss rate of 0.0396, which is consistent with the experimental value. The selectivity of FG-I at steady reaction conditions was approximately 10 percentage points lower than the Activated-I, indicating strong detrimental impact of granulation. When $\Delta X_{\text{OC}}' < 0.035$, FG-I- $\text{K}_2\text{O}(5)$ and $\text{SK}_2\text{O}(5)\text{-I}$ showed a similar value of S_{syn} as the Activated-I. The value of S_{syn} for FG-I- $\text{CaO}(5)$ was quite high at the beginning of the reaction, but declined quickly as the reaction occurred.

$\text{SCuO}(5)\text{-I}$ and FG-I- $\text{CuO}(5)$ showed better selectivity than Activated-I, with 0.98-0.99 S_{syn} until $\Delta X_{\text{OC}}'$ was less than 0.05. The addition of Cu increased the oxygen transport capacity with high fuel conversion. The synergetic effects to improve oxygen transport capacity with high fuel conversion have been observed when copper is coated on manganese ore or Hematite [28-29]. In these studies, oxygen transport capacity with high selectivity was dramatically enhanced six times. However, in this study, the increased oxygen transport capacity with high fuel conversion was solely attributed to the reduction of the CuO phase added to the OCs. The OCs added with Mn- and Ni- elements performed poorly compared to the Activated-I. Agglomeration occurred for $\text{SMn}_3\text{O}_4(7.5)\text{-I}$, which resulted in a rapid decrease in selectivity as $\Delta X_{\text{OC}}'$ was higher than 0.02.

Fig. 2 Selectivity of ilmenite-based OCs (a) K- and Ca-added, (b) Cu-, Mn- and Ni- added

3.3 In-situ gasification and combustion efficiency in coal-char fueled CLC

Comprehensive testing of the coal char-fueled CLC was performed for all of the OCs, with their instantaneous rate of carbon conversion presented in **Fig. 3**. Representative gas concentration profiles are included in the supporting materials, **S-Fig. 1**. In order to avoid the introduction of errors at the beginning and the end of reaction, the value of X_C between 0.1- 0.8 was used as the representative of steady reaction. For comparison, the results for external gasification are also presented in **Fig. 3 (a)**. In external gasification, 250.0 g sand (125-355 μ m) was used as the bed material, while the other conditions and procedure remained the same as the CLC experiments. Compared to the external gasification, the CLC experiment using Activated-I and FG-I improved the gasification rate by 35%. Among the transition metal-added OCs, SCuO(5)-I performed best, with > 100% improvement in char gasification rate compared to the external gasification experiment. Compared to other OCs, SK₂O(5)-I and FG-I- K₂O(5) significantly improved the gasification rate, and the values of r_C exhibited much higher increasing rate. These results indicate that either the char underwent a violent structural break-up or became more reactive during gasification.

Fig. 4 shows the combustion efficiencies for the same CLC experiments in **Fig. 3**. With the exception of FG-I and FG-I-NiO₂ (2.5), all other OCs demonstrated stable combustion efficiency over the reduction period. Approximately 0.95 of η_{syn} was obtained for SK₂O(5)-I, FG-I-K₂O(5), and SCuO(5)-I OCs. For FG-I and FG-I-NiO (2.5) OCs, η_{syn} varied between 0.65-0.70 at steady reaction conditions. These results indicate that the two OCs were not well suited for coal-fueled CLC. All other OCs, including FG-I-CaO(5), FG-I-CuO(5), SMn₃O₄(7.5)-I, FG-I-Mn₃O₄(7.5) and SNiO₂(2.5)-I had combustion efficiencies similar to Activated-I.

Fig. 3 Instantaneous rate of carbon conversion in CLC experiments using different ilmenite-based OCs: (a) K- and Ca-added, (b) Cu-, Mn- and Ni- added.

Fig. 4 Combustion efficiency of CLC experiments using different ilmenite-based OCs: (a) K- and Ca-added, (b) Cu-, Mn- and Ni- added.

3.4 Performances OCs in multi-redox cycles

Three samples, SK₂O (5)-I, FG-I- K₂O (5), and SCuO(5)-I, showed the most desirable performance. So these samples were selected for further study and subjected to 20 redox cycle of CLC experiments for better understand their behaviors in long-term operation. The OC's performance changes with redox cycle, and can be represented by the average carbon conversion rate ($\bar{r}_c$) and combustion efficiency ($\bar{\eta}_{syn}$) during consecutive reduction. These results, along with that of the Activated-I, are shown in **Fig. 5**. The values of $\bar{r}_c$ and $\bar{\eta}_{syn}$ were collected when X_c varied between 0.1-0.8. The results showed that the reactivity of the modified OCs with coal char were roughly stable over 20 redox cycles. After each cycle, the OC was fully regenerated, and this regeneration contributed to combusting a high percentage of carbon and maintaining their high reactivity. A slight activation process was observed for Activated-I in the first 5 cycles, and the OC's reactivity was maintained thereafter. It is obvious that the structure of the starting materials were not well stabilized even after 5 redox cycles with gaseous fuel. Here, the natural activation of the ilmenite OC, due to Fe₂O₃ segregating from Fe₂TiO₅, occurred at the cost of oxygen transport

capacity during the redox cycle [9]. Furthermore, the value of η_{syn} for Activated-I slightly increased from 0.88 to 0.90 after 20 cycles. Less activation was observed for SCuO (5)-I during 20 cycles. As will be shown, the formation of Cu-Ti-O compound on the particle surface improved the OC's reactivity and the physical stability. The value of η_{syn} for SCuO (5)-I was improved by 2.0 percentage points during the first five cycles, and remained constant at 0.97 during subsequent cycles. The average combustion efficiency of SK₂O (5)-I and FG-I- K₂O (5) increased to 0.98 after 20 cycles. Considering high combustion efficiency was realized for these two fresh samples (SK₂O (5)-I and FG-I- K₂O (5)), this increase should be a substantial improvement. Here, the increase in combustion efficiency may be due to their modified thermodynamics during consecutive cycle.

Fig. 5 Cyclic performances of the selected OCs in CLC experiments: (a) average carbon conversion rate, (b) average combustion efficiency

3.5 Discussion

3.5.1 Potential in improvement of gasification rate and combustion efficiency

The chemical processes in the FR are char gasification, OC reduction and the WGSR. Coal char is first gasified into an intermediate syngas containing CO, H₂ and CO₂. These reducing components are simultaneously converted to CO₂ and H₂O by OCs surrounding the coal char particles. The gasification rate is improved with lowered inhibition of CO and H₂ as these gases are quickly oxidized by the OCs [30]. According to this reaction regime, the gasification rate can be correlated to the OC's reactivity. As shown in Fig. 6, the value of $\bar{r}_c$ from different CLC experiments were plotted against the average OC reduction rates obtained from the TGA apparatus. Here, the average OC reduction rates ($\bar{r}_{\text{OC}}$) are time-averaged during the initial reduction period corresponding to $X_{\text{OC}}=0.985-1.0$. This is because the theoretical oxygen consumption for full fuel combustion in CLC experiment yields approximately 1.5% of OC weight loss. The result of external gasification was given under the assumption that sand was absent of lattice oxygen for fuel combustion. With the exception of SK₂O (5)-I and FG-I- K₂O (5), there is a clear trend of increasing $\bar{r}_c$ with $\bar{r}_{\text{OC}}$ for all of the other OCs. So $\bar{r}_c$ is related to $\bar{r}_{\text{OC}}$ via a linear relationship

$$\bar{r}_C = a + b \cdot \bar{r}_{OC} \quad (7)$$

Where a and b represent $\bar{r}_C$ of the external gasification and the fitting linear rate constant, which were estimated as 0.00259 and 0.0195, respectively for this study. Eq. (7) reveals how the OCs' reduction reactivity influences the in-situ gasification of CLC if the above reaction regime is followed. Obviously, the values of a and b depend on the type of coal char and OCs.

Fig. 6 Correlation between the average carbon conversion rates in CLC experiment and average OC reduction rate obtained from the TGA.

Fig. 7 Correlation between the average combustion efficiency in CLC experiments and the average selectivity from the fixed bed reactor

A large deviation of the K-added OCs from the functionality (Eq. (7)) suggests a different mechanism is involved during coal char gasification. The high reduction reactivity of the K-added OCs only explains part of the improved in-situ gasification. However, as indicated by the data points of 4 and 5 (Fig. 6), the increased OC reduction rate could not account for all the increment of gasification rate.

The value of $\bar{\eta}_{syn}$ for different CLC experiments compared to the average selectivity obtained from the fixed bed reactor, are presented in Fig. 7. This plot illustrates how the OC's selectivity influences the intermediate syngas conversion in CLC under the fluidization regime. The general trend showed that the difference between $\bar{\eta}_{syn}$ and $\bar{S}_{syn}$ increases rapidly as $\bar{S}_{syn}$ decreases. The best performing OCs (SK₂O (5)-I, FG-I- K₂O (5) and SCuO (5)-I) possess a selectivity > 0.98, and $\left(\bar{S}_{syn} - \bar{\eta}_{syn}\right)$ of 0.02-0.03. When $\bar{S}_{syn}$ was

lower than 0.90, the value of $\left(\bar{S}_{syn} - \bar{\eta}_{syn}\right)$ increased rapidly to approximate 0.20. The value of $\bar{S}_{syn}$ obtained

from the fixed bed reactor, reflects the syngas conversion under ideal conditions. Under these conditions, wet syngas are gradually converted as it moves across the bed, and this allows the syngas have enough time to react with the OCs. The value of $\bar{\eta}_{syn}$ from the CLC experiments describes the intermediate syngas conversion where the reaction between the two solids (coal char and OCs) occurs via the phase transfer of intermediate gas. Thus, the value of $\left(\bar{S}_{syn} - \bar{\eta}_{syn}\right)$, to a large extent, describes the extent of incomplete gas

phase transfer between char and the OC. **Fig. 7** reveals that the improvement in OC's selectivity significantly diminish the impact of the incomplete gas phase transfer in CLC.

3.5.2 Possible solid-solid reaction between OCs and coal char

The direct solid-solid reaction between OC and coal char, or the catalyzed char gasification arising from the addition of K, possibly make contributions to the promoted gasification of CLC when SK_2O (5)-I or $\text{FG-I-K}_2\text{O}$ (5) was used as OCs. During the catalyzed gasification mechanism, potassium elements in OCs are gradually vaporized at high temperature, and deposit on the surface of the char to catalyze gasification [7]. If this is the case, the potassium concentration of the OCs should decrease during operation. However, compare to the fresh sample, the used OCs after 20 redox cycles do not show observable loss of potassium fraction. So the catalyzed gasification mechanism can be excluded in this study. For the SCuO (5)-I, gasification could be improved by the oxygen uncoupling effects where lattice oxygen is released into the gas phase to react with the solid fuel [31]. The CLC experiment revealed that oxygen concentration in sweeping gas during the inert period of CLC was not as high as expected when SCuO (5)-I was used as OCs. Based on these results, the pathway of oxygen uncoupling was also excluded.

Fig. 8 Gas concentration profile during the experiment of solid-solid reaction between PRB coal char and SCuO (5)-I.

Fig. 9 Coal char conversion rate due to the solid-solid contact reaction between PRB char and different OCs.

A series of tests was performed to validate the role of the solid-solid reaction between OCs and coal char during in-situ gasification of CLC. Sand, Activated-I, SK_2O (5)-I, $\text{FG-I-K}_2\text{O}$ (5), and SCuO (5)-I were selected for further study. The operational conditions remained the same as the CLC experiment, with the exception of fluidization gas, which was composed of only 4.0 NL/min N_2 in the experiment of solid-solid reaction. When sand or Activated-I was used as bed materials, a very small amount of carbon-containing gas were observed during the initial char devolatilization (< 45 s). However, after this period, no carbon-containing gas was present in the exiting gas, indicating the absence of the solid-solid reaction. The experiment using SK_2O (5)-I, $\text{FG-I-K}_2\text{O}$ (5), or SCuO (5)-I, experienced an appreciable amount of coal char oxidation in the N_2 stream, with only CO_2 present in the exit gas. This observation is a manifestation of the direct solid-solid reaction between OC and coal char [24]. As an example, **Fig. 8** shows the gas concentration profile during the solid-solid reaction between coal char and SCuO (5)-I. **Fig. 9** shows the instantaneous rate of carbon conversion from the solid-solid reaction for different bed materials. Compared to in-situ gasification in CLC, the solid-solid reaction between SK_2O (5)-I, $\text{FG-I-K}_2\text{O}$ (5), or

SCuO (5)-I and coal char was slow, but proceeds to a high level of carbon conversion. The relative reaction rate at a given carbon conversion (α - the ratio of the carbon conversion rate due to the solid-solid reaction to that of CLC) can be used to describe the role of the solid-solid reaction (the detailed definition can be found elsewhere [24]). Using this calculation, the average value of α , in the range of $X_C = 0.1-0.6$, was 3.3% and 3.2% for SCuO(5)-I OC and FG-I- K₂O (5), respectively. Therefore, the contribution of the direct solid-solid reaction in CLC is likely negligible for these two OCs. The average value of α for SK₂O (5)-I is 28.5%. However, this is not enough to account for the improvement of char gasification. These results indicate that the direct solid-solid reaction is not the sole and determining pathway for the significant improvements of gasification in CLC when SK₂O (5)-I or FG-I- K₂O (5) is used.

3.5.3 Water gas shift reaction

Due to the thermodynamics and incomplete reaction of CLC, there is a level of unconverted fuel gas in the CO₂/H₂O stream. In the FR, the WGSR tries to shift the gas components towards the equilibrium of that condition, and the rate of this reaction plays a vital role [32-33]. OC particles in the bed section (or in their reduced form) may catalyze the WGSR. **Fig. 10** illustrates the catalytic functions of the most promising OCs during the first and the 20th cycles of the CLC experiments, where the value of J was calculated according to Eq. (6). Fresh Activated-I did not promote the WGSR compared to sand during the external gasification. The used Activated-I in the 20th cycle weakly prompted the WGSR, and Fe₃O₄ phase created during the redox cycles catalyzed the reaction. The fresh SK₂O (5)-I showed strong a catalytic effect, with the value of J (0.53) very close to the equilibrium constant at 950 °C, K_{eq} (0.68). This meant that the WGSR in the bed zone proceeded rapidly towards equilibrium. Fresh FG-I- K₂O (5) was less catalytic than fresh SK₂O (5)-I, but its performances in the 20th cycle was approximate to SK₂O (5)-I. The catalyzed in-situ WGSR in the bed zone may play a role in enhancing CLC gasification. The catalyzed in-situ WGSR among the intermediate syngas lowers CO content and increases the concentration of H₂. It allows more H₂ to react with the OCs at higher rate because H₂ is the more reactive reducing agent, as shown in **Fig. 1**. In return, the quick consumption of the gasification inhibitors increased combustion efficiency and the gasification rate. This mechanism is partially confirmed by the fact that CLC experiments of two K-added OCs presented a combination of high gasification rate and strong in-situ WGSR effect.

Fig. 10. The values of J during CLC experiments using different OCs (the equilibrium constant of WGSR at 950 °C was calculated by $\log K_{eq} = -2.4198 + 0.0003855T + \frac{2180.6}{T}$ [34]).

3.5.4 Physical and chemical change during multiple redox cycles

For the most promising OCs, the decay of K or Cu elements, agglomeration or sintering, coal ash contamination, and change in morphology are the major concerns for long term operation. **Fig. 11** and **Table 4** show the SEM images and chemical compositions for the fresh and used OCs, respectively. The BET surface area, mechanical strength, and XRD analyses are listed in **Table 1**. The fresh Activated-I possesses a very dense structure (**Fig. 11 (a)**), and is composed of Fe_2TiO_5 and a small amount of Fe_2O_3 . During 20 redox cycles, Activated-I particles experienced strong rounding and gradual formation of external layer. The formation of the external layer was the result of Fe-element segregation at the surface of the particles from Fe_2TiO_5 during reduction [9]. The external layer became Fe-element enriched, while the internal core was Ti-element enriched after 20 redox cycles. Compared to the fresh sample, the used Activated-I had much stronger characterization peaks of Fe_2O_3 phase in the XRD spectrum. The external layer of the used sample cracked, and parts of this external layer fell from the internal core. In **Fig. 11 (b)**, a small piece of the external layer (in the right side) detached from the particles and exposed the internal core. The dense external layer was composed primarily Fe-element, and the internal core was composed of high and increasing concentration of Ti-element. Furthermore, the existence of the external layer increased the fragility of the particles.

Compared to the Activated-I, K-added OCs are composed of a considerable amount of free Fe_2O_3 crystalline phase and less Fe_2TiO_5 . K-elements in SK_2O (5)-I and FG-I- K_2O (5) were immobilized as $\text{K}_2(\text{Ti}_8\text{O}_{17})$ and $\text{K}_{1.46}\text{Ti}_{7.2}\text{Fe}_{0.8}\text{O}_{16}$. Over 20 redox cycles, the K_2O fraction did not decline for the two K-added OCs, indicating that K elements in these OCs were quite stable. The addition of K-elements and the abundance of SiO_2 in coal ash (see coal ash analysis in **Table 3**) seem to increase the risk of chemical reaction between OC and coal ash. In **Fig. 11 (d)** and **(f)**, ash-like melted granules were seen on the particle surfaces. Furthermore, SiO_2 concentration of the used SK_2O (5)-I and FG-I- K_2O (5) increased by 2% points during this time. The SEM images revealed the coating of the K-element seriously altered the changing trend of particle morphology during multiple redox cycles. For the fresh SK_2O (5)-I (**Fig. 11 (c)**), the granular particles reacted with some of K_2O and underwent considerable sintering, while the remainder of K_2O was homogeneously distributed on the particle surface. An Fe-rich external shell did not form on the surface of the used SK_2O (5)-I. Instead, the formation of big crystals (1-2 μm) and macropores completely reconstructed the surface area of the particles, and as a result, the crushing strength decreased from 4.7 N to 3.2 N after 20 cycles.

The Cu-element coating effectively hindered the formation of the external layer due to Fe-element segregation in multiple redox cycle. For fresh SCuO (5)-I, Cu-elements were evenly distributed on the particle surface. In 20 cycles, the particle surface underwent considerable sintering, and average diameter of the granules increased considerably from 1 μm to 5 μm . SEM-EDX analysis reveals that Cu-, Ti- and Fe-elements were evenly distributed on the used particles (**Fig. 11 (h)**). Cu_3TiO_4 , created via the reaction between CuO and ilmenite during calcination, protected Fe_2TiO_5 from direct decomposition to Fe_2O_3 and TiO_2 during reduction. Compared the fresh sample, the used SCuO (5)-I particles possessed a very dense structure and maintained high mechanical strength.

(a) Activated-I (Fresh)

(b) Activated-I (used)

(c) SK₂O(5)-I (Fresh)

(d) SK₂O(5)-I (used)

(e) FG-I- K₂O(5) (Fresh)

(f) FG-I- K₂O(5) (used)

(g) SCuO(5)-I (Fresh)

(h) SCuO(5)-I (used)

Fig. 11. SEM images of ilmenite-based OCs before and after 20 redox cycle

Table 4 Chemical composition of ilmenite-based OCs

Chemical Composition	Activated-I		SK ₂ O(5)-I		FG-I- K ₂ O(5)		SCuO(5)-I	
	Fresh	Used	Fresh	Used	Fresh	Used	Fresh	Used
Fe ₂ O ₃	52.66	52.41	49.63	48.12	49.71	48.07	51.19	52.19
SiO ₂	5.39	5.21	5.58	7.33	5.19	7.01	4.59	4.44
Al ₂ O ₃	3.57	4.52	4.04	4.93	4.09	4.46	3.44	3.74
TiO ₂	33.27	32.51	29.34	27.84	29.85	28.33	31.42	31.48
CaO	0.8	0.77	0.87	1.04	0.81	1.17	0.82	0.73
MgO	3.19	3.16	3.01	3.02	2.96	3.15	2.89	2.91
Na ₂ O	0.29	0.29	0.395	0.43	0.47	0.40	0.33	0.28
K ₂ O	-	-	5.19	5.08	4.95	5.17	-	-
CuO	-	-	-	-	-	-	4.85	3.99
Balance	0.83	1.13	1.75	2.21	1.97	2.24	0.47	0.24

4. Conclusions

- (1) The addition of K significantly improved the reactivity of ilmenite OCs with wet syngas and coal char. These CLC experiments achieved combustion efficiency > 95%. When K-added ilmenite OCs were used in CLC experiments, the high reduction reactivity, the direct solid-solid reaction between coal char and OCs, and the catalytic function for the WGSR, make contributions to the improvement of the in-situ gasification.
- (2) SCuO(5)-I OC is an attractive oxygen carrier for the coal-fueled CLC. The coating of Cu-element enhanced the OC reactivity, oxygen transport capacity, and selectivity with wet syngas. Compared to external gasification, CLC experiments using Cu-coated OCs, improved the gasification rate > 100%. The combustion efficiency of CLC was significantly enhanced to 95%, comparable to 87.5% of combustion efficiency using the activated ilmenite OCs. The Cu-element coating effectively hindered iron-element segregation, and the particle integrity was maintained during multiple redox cycles.
- (3) Ca-, Ni- and Mn-added ilmenite-based OCs did not show promising prospects for the coal-fueled CLC.
- (4) Some key considerations for OC development as follows: a.) The evaluation of the OC reactivity must include the influence of steam in the fuel gas. Steam is an essential component for enhancing gasification of CLC, but significantly inhibits OC's reduction reaction. b.) The in-situ gasification rate of CLC can be correlated with the OC's reduction reactivity. In this correlation, increases in OC's reactivity showed less improvement of gasification rate than expected because char gasification is the limiting step. c.) The OC ability of converting syngas to CO₂ and H₂O is an important performance for the full combustion of intermediate syngas in the fuel reactor. d.) The strong OC catalytic function for the WGSR could be an effective way to improve gasification rate and combustion efficiency of coal-fueled CLC.

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