Catalytic chemical looping combustion of carbon with an iron-based oxygen carrier modified by K_2CO_3: Catalytic mechanism and multicycle tests

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ABSTRACT

One of the major obstacles of chemical looping combustion (CLC) with solid fuels is the low reaction rate of solid fuels with an oxygen carrier. Alkali metal catalysts can be used to enhance the reaction rate. In this work, the catalytic reduction mechanism of a K_2CO_3 modified iron-based oxygen carrier by activated carbon (AC) and the multicycle CLC tests were investigated. The results confirm that the deep reduction of K_2CO_3 added iron-based oxygen carrier occurred at a high rate. The energy dispersive spectrometer (EDS) analysis shows that the catalytically active species of K_2CO_3 migrated from the oxygen carrier to the surface of AC during reduction, which could then catalyze the rate-limiting step ($C-CO_2$ reaction) of the reduction process. Besides the catalytic effect of K_2CO_3, a remarkable autocatalytic effect of iron oxide itself on the reduction was also observed. The active species could also travel back to the oxygen carrier after reduction, which guaranteed the persisting catalytic effect in the multicycle tests. The loss of potassium primarily contributed to the deactivation of the oxygen carrier, but this deactivation can be partly retrieved and improved by the supplement of K_2CO_3.

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1. Introduction

It is costly to separate CO_2 and atmospheric N_2 from the flue gas of conventional air combustion due to the high energy penalty of gas–gas separations. In general, the gas–solid separations are much easier than the gas–gas separations. If the separation of N_2 and CO_2 can be substituted by gas–solid separations, the cost can be potentially reduced. Chemical looping combustion (CLC) utilizes two gas–solid separations to replace the CO_2–N_2 separation of the conventional air combustion, as shown in Fig. 1 [1]. Two essential reactors are involved in a CLC system: an air reactor and a fuel reactor. The oxygen carrier is circulated between these two reactors during operation. The first gas–solid separation aims to separate N_2 and the oxidized oxygen carrier from the air reactor, where the gaseous O_2 in air is "stored" into the oxygen carrier in the form of lattice oxygen. The second gas–solid separation is designed for CO_2 and the reduced oxygen carrier from the fuel reactor, within which the lattice oxygen transfers from oxygen carrier to fuel to produce CO_2. With this arrangement, fuel can be burned by air while the CO_2 and atmospheric N_2 are inherently separated. Recently, CLC of solid fuels has gained an increasing interest [2–6].

In terms of CLC of coal with an iron-based oxygen carrier, three approaches are available: coal direct CLC, syngas-CLC, and in-situ gasification CLC (iG-CLC) [5,7]. An advantage of coal direct CLC is the

relatively high oxygen transport capacity (OTC) as the Fe_2O_3 can be reduced to FeO/Fe [5]. However, a disadvantage is the low reaction rate, especially when the Fe_2O_3 is deeply reduced [8]. To overcome this disadvantage, syngas can be used to reduce the oxygen carriers, with either ex-situ or in-situ gasification approach. With syngas-CLC, significant extra energy input is needed for the air separation unit (ASU) [9]. To avoid the requirement of ASU, iG-CLC was proposed, where the fuel particles are in-situ gasified by CO_2 and/or H_2O in the presence of oxygen carriers [7,10]. Compared to coal direct CLC, the reduction rate can be improved by iG-CLC, but the OTC is decreased because the reduction of Fe_2O_3 is thermodynamically limited to the form of Fe_3O_4 [11,12].

The solid inventory of a CLC process is directly affected by the reaction rate and the OTC of the oxygen carrier. For the reactivity enhancement of iG-CLC and coal direct CLC, alkali metal catalysts are usually used. Gu et al. found that the reduction rate of iron ore oxygen carrier in iG-CLC could be improved by K_2CO_3 loading, and suggested that this improvement was mainly caused by the accelerated char gasification and water–gas shift reaction [13]. The solid inventory of a CLC process is expected to be significantly decreased if the high reaction rate and high OTC of oxygen carrier are simultaneously satisfied. Our previous research indicated that the reduction rate of iron oxide oxygen carrier of coal direct CLC could be remarkably enhanced by the addition of alkali metal carbonates (high reactivity); meanwhile, the Fe_2O_3 can be reduced to an oxidation state of FeO/Fe (high OTC), suggesting that catalytic CLC was an effective method of coal combustion with a low solid inventory [14].
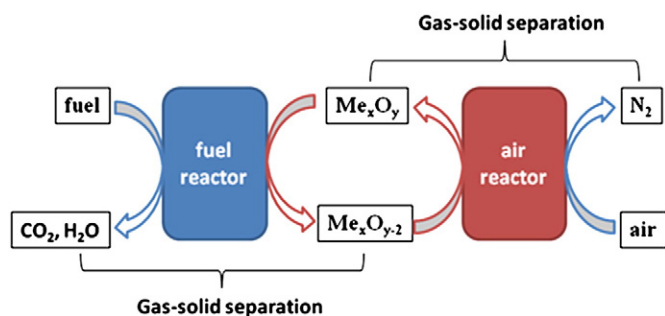
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Fig. 1. Schematic diagram of chemical looping combustion (CLC).

Even though there are some researches focusing on the effects of alkali metal on iron-based oxygen carrier, the catalytic mechanism has not been addressed in more detail, especially in the following aspects: (1) how the alkali metal initially loaded on oxygen carrier catalyzes the char gasification; (2) the catalytic effect of reduced iron oxide itself on char gasification in the presence of alkali metal addition; and (3) the maintained catalytic effect in the multicycle operation. Hence, this work aims to investigate these aspects of the catalytic CLC of activated carbon (AC) with an iron-based oxygen carrier modified by K_2CO_3.

2. Experimental section

The oxygen carrier used in this work consists of 70 wt.% Fe_2O_3 and 30 wt.% ZrO_2 (denoted as Fe70Zr30), which was synthesized by a co-precipitation method at room temperature using the following procedures: First, 85.14 g of $Fe(NO_3)_3 \cdot 9H_2O$ (98.5%, Sinopharm Chemical Reagent Co., Ltd., China) and 25.00 g of $Zr(NO_3)_4 \cdot 5H_2O$ (99.0%, Sinopharm Chemical Reagent Co., Ltd., China) were mixed in the de-ionized water. Then, this solution and $NH_3 \cdot H_2O$ were added to 100 mL of de-ionized water dropwise under vigorous stirring. The pH during precipitation was kept at a value of 9. After precipitation, the product was filtered and the precipitate was washed using the de-ionized water and then air dried overnight at 110 °C. Finally, the precipitate was calcined at 1000 °C for 8 h in muffle furnace. The obtained oxygen carrier was crushed and sieved to a particle size below 180 μm.

The K_2CO_3 modified Fe70Zr30 oxygen carrier was prepared by impregnation as follows: a desired amount of K_2CO_3 (99.0%, Tianda Chemical Reagent Factory, China) was dissolved in de-ionized water and then this solution was slowly added to Fe70Zr30 particles; after ultrasonic treatment for 60 min, the slurry was air dried at 110 °C for 12 h. The loading ratios of K_2CO_3 were varied from 0, 2, and 6 wt.% in terms of K_2CO_3/Fe_2O_3. The K_2CO_3 loaded Fe70Zr30 was referred to Kx-Fe70Zr30, where x represents the loading amount of K_2CO_3. The oxygen carrier was physically mixed with AC (Sinopharm Chemical Reagent Co., Ltd., China) with a mass ratio of 9/1 (Fe70Zr30/AC). The proximate and ultimate analyses of AC are listed in Table 1.

The reactivity of oxygen carrier was investigated by a Setaram Setsys TGA instrument. About 25 mg of the mixture was heated in a platinum crucible under N_2 atmosphere (100 mL/min) from 30 °C to 850 °C with a rate of 10 °C/min. Then, the mixture was held at 850 °C for 40 min before the carrier gas was switched to air (100 mL/min) for a 10 min oxidation.

The multicycle CLC tests were simulated in a fixed-bed reactor (as shown in Fig. 2). The experimental procedures are briefly described as

Table 1
Proximate and ultimate analyses of activated carbon (AC).

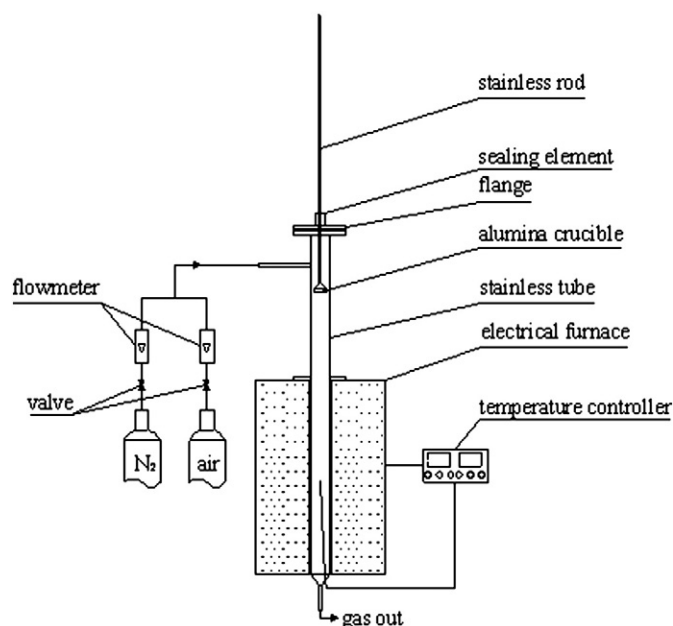| Sample	Proximate analysis (wt.%, air-dried basis)				Ultimate analysis (wt.%, air-dried basis)				
	M	V	A	FC	C	H	O	N	S
AC	1.53	14.23	1.85	82.39	83.1	2.22	9.02	0.62	0.16

Fig. 2. Schematic diagram of the fixed bed reactor for multicycle CLC tests.

follows: About 1.2 g of mixture was loaded into a cylindrical alumina crucible (35 mm i.d. × 10 mm height). Then, the crucible was placed into the cooler chamber of the reactor. After flushing the reactor with a continuous stream of N_2 for 60 min, the crucible was lowered quickly into the reaction zone for 40 min under N_2 atmosphere. Then, the carrier gas was switched to air for a 10 min oxidation. Finally, the crucible was lifted rapidly to the cooler chamber where the crucible was quenched under a N_2 stream. The reaction temperature was set to 850 °C and all the flow rates of the purge gases were kept at 200 mL/min. After the crucible was cooled, the residue was taken off and mixed with another dose of AC to prepare the next redox cycle. Meanwhile, about 25 mg of the newly prepared mixture was transferred to the TGA to assess the redox behavior of oxygen carrier in every two cycles.

X-ray diffraction (XRD) patterns of the oxygen carriers were collected on a RIGAKU D/max-rB X-ray powder diffractometer using Cu Kα radiation (40 kV, 100 mA, Kα1 = 0.154 08 nm). A JEOL field emission scanning electron microscope (FESEM, JSM-7001F) coupled with an energy dispersive spectrometer (EDS, BRUKER) was used to characterize the surface morphology and the elemental mapping of the oxygen carriers. The element contents of K were analyzed by an inductively coupled plasma-atomic emission spectrometer (ICP-AES, iCAP 6300, Thermo Fisher).
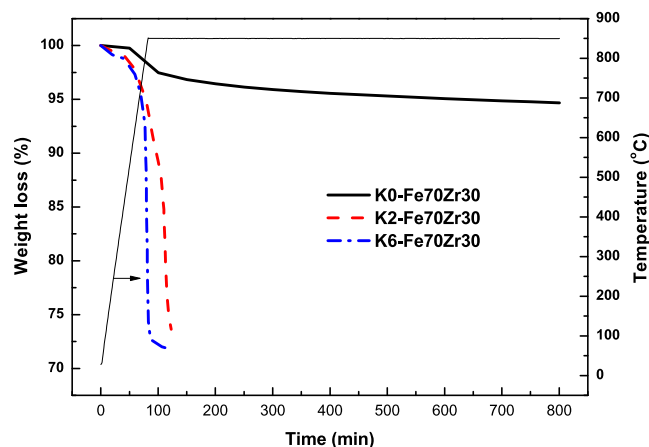

Fig. 3. Weight loss of Kx-Fe70Zr30 oxygen carrier with AC under N_2 atmosphere.