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Research article

Understanding of the oxygen uncoupling characteristics of Cu—Fe composite oxygen carriers for chemical-looping gasification

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ABSTRACT

A Cu—Fe oxygen carrier (OC) with oxygen uncoupling capability is proposed to be applied in chemical-looping gasification with oxygen uncoupling (CLGOU) technology to increase the gasification rate. Density functional theory analysis shows that a chemical reaction occurs after Cu_4O_4 cluster adsorption onto α - Fe_2O_3 (001) surface. Extension of bond length and transfer of charge indicate the composite oxide has been activated. An optimal molar ratio of 2:1 of CuO to Fe_2O_3 is determined for the preparation the OC and the oxygen transport capacity is determined at 3.65 wt% with a starting oxygen uncoupling temperature is 749.5 °C. The composite OC exhibits good low-temperature oxygen uncoupling characteristics. This OC exhibits stable behaviour and satisfactory oxygen recyclability over 15 consecutive redox cycles at 900 °C / 700 °C oxygen uncoupling and absorbing temperatures. The high stability is corresponding to the calculation result (high adsorption energy of CuO onto Fe_2O_3). And oxygen uncoupling rates are much higher than the lower limit (0.4 wt%/min) for cracking. The chemical phases and surface micromorphology all retain stable after cycles. Using combined Coats-Redfern and Malek method, the oxygen uncoupling kinetic model of Cu—Fe OC is determined as a shrinking core model ($m = 3$).

1. Introduction

Waste resource utilization and climate change are the most compelling problems of today's world [1]. Therefore, finding and exploiting alternative energy sources has become a hot topic in the energy and environmental research fields. Biomass, a clean and renewable energy, has been the fourth largest energy source after oil, coal and natural gas [2]. Compared with coal, the sulphur and ash contents of biomass are much lower. Besides, biomass is the only renewable source of carbon, which can solidify CO_2 from the air and achieve net zero CO_2 emissions [3,4]. Clean and efficient use of biomass will effectively help alleviating energy shortage and protect ecology.

At present, the utilization of biomass mainly includes bio-briquette fuel, bio-syngas, and bio-liquid fuel [5]. And thermochemical transformation, physical transformation and biological transformation are the main methods to convert biomass to biofuel. Among the thermal

chemical transformation processes, biomass gasification has the highest industrial application prospect with advantages of a high gas production rate, a high degree of automation and operation at large scale [6]. By 2015, the global biogas output is about 57 billion m^3 , of which the annual biogas output in Germany is more than 20 billion m^3 . The Swedish biogas meets 30% of the national demand for vehicle gas [7]. During gasification, biomass is converted to easily transportable gas fuels under high heat demand, and the main reaction products are H_2 , CH_4 , CO, CO_2 and a small amount of other hydrocarbons [8]. In this process, the gasification agents such as air, O_2 , H_2O and CO_2 are used. However, the presence of N_2 in the gas products greatly reduces the heat value of the produced syngas when air is used as gasification agent. Pure oxygen as the gasification agent has benefits of a high carbonization rate and high concentration of combustible gas, but the high cost of current oxygen production technologies adversely affect the economy of biomass gasification by pure oxygen hampering its exploitation [9].

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Fig. 1. Schematic of CLGOU.

To find a suitable oxygen source for biomass gasification, the chemical-looping gasification (CLG) was proposed [10]. During gasification, fuel is gasified by lattice oxygen in oxygen carrier (OC) following syngas mainly consists of CO and H₂, maintained by controlling the ratio of the OC and fuel. Subsequently, during oxidation, the reduced OC absorbs oxygen to bring the OC back to the oxidized state. The most expected advantages are: i) OC provides lattice oxygen for gasification, and a separate oxygen unit is omitted; ii) the heat released can be carried out over by the OC from air reactor to gasification reactor, thus acting also as a heat carrier; iii) the metal OC can catalyze reactions with tar, which can reduce the tar content [11–13].

The OC links the two separated reactors and is the key for a good performance of CLG. Extensive researches on OCs for CLG have been carried out. Huang et al. found that the carbon conversion rate and syngas production rate using CLG technology increased by 7.47% and 11.02% respectively, compared with traditional steam gasification [14]. They also studied the Ni–Fe composite OC for CLG at 1200 °C, and their results showed that NiFe₂O₄ promoted the gasification of fixed carbon [15]. Sozen et al. carried out CLG experiments using an Fe-based OC and found that the H₂ and CO yields, carbon transformation rate all enhanced with an increase in the gasification temperatures [16]. Zhao et al. utilized a Cu-based OC to gasify biomass at 600–850 °C and found that the Cu-based OC could prompt the carbon conversion and reduce the C₂H_m and tar in the syngas [17]. Ge et al. used natural hematite OC and determined the optimal gasification parameters: 860 °C gasification temperature, 1.0 steam-to-biomass ratio and 40 wt% hematite mass percentage [18].

The reported studies on CLG mainly focused on the reaction between lattice oxygen and fixed carbon as well as the catalysis of tar. In this process, the solid OC reacts with solid biomass char or fixed carbon directly. Due to the restriction of diffusion, heat and mass transfer, the solid-solid gasification reaction does not occur at an appreciable rate. The low gasification rate of solid fuel is also the limit of chemical-looping combustion (CLC) [19–21]. In solve this limit, a novel chemical-looping with oxygen uncoupling (CLOU) technology was put forward in 2005 [22–24]. OC first undergoes oxygen uncoupling and releases gaseous oxygen. And solid fuels are directly gasified by gaseous oxygen released. Solid-solid combustion of OC and fuel converts to gas-solid combustion of released gaseous oxygen and fuel. Thus, combustion efficiency is significantly increased. Based upon the CLOU concept, in this study the OC with oxygen uncoupling capability is proposed to be applied in the CLG technology. A schematic of the chemical-looping gasification with oxygen uncoupling (CLGOU) is shown in Fig. 1.

In CLGOU technology, the gasification agent is the gaseous oxygen released by OC and steam. O₂-steam gasification of biomass is a relatively mature technology and many works on O₂-steam gasification have been carried out. Meng et al. investigated the effects of operational conditions on the tar formation in O₂-steam gasification at temperatures of 730–820 °C and found that bed materials affected the tar

decomposition [25]. Huynh et al. studied the characteristics of O₂-enriched air and steam biomass gasification process at 800 °C and concluded that this process favors the production of combustible gas components in the syngas [26]. Fu et al. indicated that the biomass gasification could be completed below 800 °C when enriched air and steam were used as fluidizing and oxidizing agents [27].

Based upon the above analysis, the OC, which has a low reduction temperature is required for the of CLGOU technology. CuO, Mn₂O₃ and Co₃O₄ are commonly used in CLOU. Among these, the Cu-based OC has the highest reactivity and oxygen transport capacity of CuO is 10 wt%, but the uncoupling temperature is also high (>800 °C). For a Mn-based OC, the uncoupling temperature is the lowest (~600 °C) and the oxygen transport capacity of Mn₂O₃ is 3.4 wt%. However, it suffers from oxidation due to the thermodynamic limits. The highest reaction heat and price, as well as the safety and environmental concerns restrict the scale-up application of Co-based OC [28–30]. The oxygen transport capacity of Co₃O₄ is 6.6 wt%. CuO and Fe₂O₃ are mostly used in CL technologies. More importantly, they all have the catalysis on the gasification reaction as well as the reduction of tar [3,18,31–33]. Many works have proved that elemental composition can effectively improve the thermodynamic properties of oxides [34–39]. In this study, we attempt to develop a typical Cu–Fe composite OC and investigate its feasibility for CLGOU.

This study focuses on oxygen uncoupling characteristics and mechanism of the Cu–Fe combined OC. Density functional theory (DFT) calculation was introduced to investigate the activity and stability of CuO onto α -Fe₂O₃ (0 0 1) surface. In the following parts, the Cu–Fe composite OC was prepared, and the oxygen uncoupling performances viz. reactivity, kinetic and stability, were investigated experimentally. The optimal mole ratio of CuO and Fe₂O₃ was determined based upon the oxygen uncoupling temperature and oxygen transport capacity. The redox reactivity under several critical operating parameters, viz. oxygen concentration and heating rate was investigated by thermogravimetric analysis. Stability of Cu–Fe composite OC over several consecutive redox cycles was investigated followed by BET, XRD, and SEM characterizations. Finally, a kinetic model of the oxygen uncoupling reaction was developed from the obtained experimental data. The oxygen uncoupling reactivity, kinetics, and stability data of this type of OC is the basis for the further development and design of a CLGOU system and gasification reactor.

2. Computational and experimental section

2.1. Computation module and parameter setting

In recent years, DFT calculation has successfully gotten the interaction information of composite materials from an electronic and atomic level. In this paper, the aims of DFT calculations were mainly obtain the activity and stability of CuO/Fe₂O₃ adsorption system theoretically. In

Table 1
Parameter settings.

Parameters	Values
Energy tolerance	1.0E-5 Ha
Force tolerance	0.002 Ha/Å
Maximum iteration steps	500
Maximum step length	0.3 Å
SCF convergence	1.0E-6
Maximum displacement tolerance	0.005 Å
Smearing	0.001

our calculations, the DMol₃ module was selected, and the method used was a generalized gradient approximation (GGA) employed by the exchange-collection potential of Perdew, Burke, and Ernzerhof (PBE). Effective Core Potential (ECP) was used to replace inner electrons, and the valence electron wave function was Double Numeric with Polarization (DNP) [40–42]. The parameters settings for all calculations are summarized in Table 1.

2.2. Preparation of OC

The Cu–Fe composite OC was prepared using mechanical mixing method with analytical purity powders ($\geq 99.0\%$) of CuO, Fe₂O₃ and ZrO₂ as raw materials. ZrO₂ was used as the support. Among the suitable binders (ZrO₂, SiO₂, Al₂O₃, MgAl₂O₄, cement etc.) for OC, ZrO₂ has the advantage of high stability during redox reaction and its function is to enhance the sintering resistance characteristic of OC [43]. The whole preparation process includes: mixing, drying (80 °C for 12 h), calcining (950 °C for 6 h), squeezing and sieving (150–180 μm).

2.3. Characterization of OC

DFT calculations indicate new phases formed in the OC particles. XRD (PANalytical PW 3040/60) was used to determine phase compositions of Cu–Fe composite OC. SEM-EDX (ULTRA 55) is a useful measurement to assess the sintering resistance characteristic of OC. The specific surface area (BET, Quantachrome NOVA 1200e) affects the gas diffusion rate inside the OC particle. The crushing strength of OC is another essential characteristic, which strongly affects the long-time use of OC in fluidized bed or fixed bed. A press apparatus measured the crushing strengths of OC in this study.

2.4. Experimental set-up

Experiments were performed in a TGA (NETZSCH, STA 409 PC). In each test, ~10 mg composite material was placed in a corundum crucible. During the oxygen uncoupling process, 0.0, 7.0, 14.0, 21.0, 33.3, 50.0 vol% O₂ in N₂ mixing gases were used, and the volumetric flow was 30 ml·min^{−1}. The Cu–Fe OC was heated from room temperature to 1100 °C with heating rates of 10, 15, 20, 25 K·min^{−1}, respectively.

2.5. Data evaluation

In the DFT calculations, the binding energy (E_{bind}) refers to the difference of total energy of each substance before and after adsorption, given by [44]:

$$E_{\text{bind}} = E_{(\text{Cu}_4\text{O}_4\text{--surface})} - (E_{(\text{surface})} + E_{(\text{Cu}_4\text{O}_4)}) \quad (1)$$

where $E_{(\text{Cu}_4\text{O}_4\text{--surface})}$ is total energy of adsorption model, eV; $E_{(\text{Cu}_4\text{O}_4)}$ is energy of Cu₄O₄ cluster, eV; $E_{(\text{surface})}$ is energy of adsorption surface, eV.

During each experiment, recording the temperature and mass of the sample as a function of temperature or time, the conversion was determined via:

$$X_{\text{OC}} = 1 - \frac{M - M_{\text{red}}}{M_{\text{oxi}} - M_{\text{red}}} \quad (2)$$

where X_{OC} is the conversion of OC, %; M_{red} and M_{oxi} represent the mass of complete reduced and oxidized OC, mg; and M is the real-time mass, mg.

3. Density functional theory analysis

3.1. Optimization of Fe₂O₃ surface structure

Fe₂O₃ belongs to α type cell structure under natural conditions and α -Fe₂O₃ crystallizes in the hexagonal close-packed corundum. The space group is R-3c, which is an antiferromagnetic material. The spin direction is $\uparrow\downarrow\uparrow$. Fig. 2(a) shows a cell structure of Fe₂O₃. The theoretical value of cell parameters after optimization is $a = b = 5.035$ Å, $c = 13.720$ Å, agreeing well with the experimental value ($a = b = 5.038$ Å, $c = 13.772$ Å) [45–47].

α -Fe₂O₃ (0 0 1) surface is a low index surface with catalytic activity, and the Fe-terminated surface is the most stable. Therefore, this surface

Fig. 2. Structure of α -Fe₂O₃ cell.

Fig. 3. Structure of α -Fe₂O₃ (0 0 1) surface adsorption Cu₄O₄ cluster. (a - Initial state; b - Optimized).

is selected for calculations, and the vacuum layer is taken as 20 Å, and a (2 × 2) nine-layer supercell plate model is constructed for optimization. Fig. 2 (b) and (c) are the main view and top view of α -Fe₂O₃ (0 0 1) surface structure, respectively.

Convergence test of K-points was carried out. The results show that the differences of total energies under K-point meshes of 2 × 2 × 1, 3 × 3 × 1 and 4 × 4 × 1 are very minimal (< 10⁻³ eV) and they all show considerable accuracy. Thus, in order to save calculation time, the K-

point mesh is selected as 2 × 2 × 1, and the total energy is -1.55E5 eV.

3.2. Adsorption of Cu₄O₄ cluster onto α -Fe₂O₃ (0 0 1)

Fig. 3 (a) depicts initial position of the adsorption model. Cu₄O₄ cluster is placed above the surface of α -Fe₂O₃ (0 0 1), so that the distance between O atom at bottom of cluster and the two Fe_{3f} atoms on the surface is equal, which is 2.834 Å. After optimization, depicted in Fig. 3 (b), it can be seen that the atomic structure of the adsorption model has changed clearly, and the structure of Cu₄O₄ cluster has become distorted. The calculated binding energy is -6.14 eV and this value is higher than the binding energies of Cu₄O₄ cluster onto CuO (111) (-2.92 eV) [44], CuAl₂O₄ (100) (-4.25 eV) [44], and onto ZrO₂ (101) (-5.54 eV) [42]. It indicates chemical adsorption has taken place, and the sintering resistance characteristic of Cu-Fe composite OC should be very high.

The changes of Mulliken charge and bond length of Cu₄O₄ clusters by adsorption onto α -Fe₂O₃ (0 0 1) surface were compared. The average length of Cu & O develops from 1.983 Å in initial state to 2.343 Å after adsorption (see Table 2). The charge numbers of all of the Cu (O) atoms after adsorption have been changed. Meanwhile, the overall charge data decreases from 0 to -0.023, and the Cu₄O₄ cluster obtains some electrons from α -Fe₂O₃ (0 0 1) surface. The extending of bond length and the charge transferring also indicates the composite oxide has been activated [48].

The electronic properties are analyzed furtherly by comparing the density of states (DOS). Fig. 4 shows changes of DOS of the surface of α -Fe₂O₃ (0 0 1) before and after Cu₄O₄ cluster was loaded. The position of DOS peak remains unchanged before and after loading. However, the DOS peaks are steep at -19 ~ -16 eV, and the electron shows strong localization. The DOS peaks appear mild at -7.5-0 eV, and the electron has strong delocalization. The lower peak intensity after loading indicates that part of the electrons on the surface has been lost and

Table 2

Changes of Mulliken atom charge and bond length before and after adsorption.

Cu ₄ O ₄	Cu(1)	Cu(2)	Cu(3)	Cu(4)	O(1)	O(2)	O(3)	O(4)	Overall charge	Cu & O (Å)
Free	0.547	0.547	0.547	0.547	-0.547	-0.547	-0.547	-0.547	0	1.983
Adsorption	0.444	0.458	0.577	0.564	-0.477	-0.462	-0.541	-0.586	-0.023	2.343

Fig. 4. DOS of α -Fe₂O₃ (0 0 1) before and after Cu₄O₄ cluster loaded.

Fig. 5. DOS of Cu_4O_4 cluster before and after loading onto $\alpha\text{-Fe}_2\text{O}_3$ (0 0 1) surface.

Fig. 6. Weight loss and loss rate of Cu—Fe OC in oxygen uncoupling test.

transferred to Cu_4O_4 cluster, which is consistent with the result of the Mulliken charge analysis.

Fig. 5 shows the changes of DOS of Cu_4O_4 cluster before and after

loading onto $\alpha\text{-Fe}_2\text{O}_3$ (0 0 1) surface. The Cu_4O_4 cluster has fewer DOS peaks after loading onto $\alpha\text{-Fe}_2\text{O}_3$ (0 0 1) surface. The DOS peaks have even disappeared entirely after the position of 2 eV energy level.

Fig. 7. Conversion and mass loss rate of OC under different local oxygen concentrations.

Fig. 8. Conversion and mass loss rate of OC under different heating rates.

Moreover, the peaks are more gentle at -5 – 0 eV and electrons show strong delocalization, which shows that Cu_4O_4 cluster and α - Fe_2O_3 (0 0 1) surface have strong interaction and the activity of the adsorption system has been enhanced.

4. Experimental results analysis

4.1. Determination of mole ratio of CuO to Fe_2O_3

During the preparation of Cu–Fe OC, four-mole ratios of CuO to Fe_2O_3 were used. Their oxygen uncoupling characteristics were investigated, and the results are shown in Fig. 6. For the four samples, the starting oxygen uncoupling temperatures are similar, however, the temperatures at the point of maximum mass loss rate are different. The OC with a molar ratio CuO: Fe_2O_3 of 1:1 presents the best low-temperature oxygen uncoupling activity. The reason is that the molar concentration of the active phase of CuFe_2O_4 in the OC is the highest at a molar ratio CuO: Fe_2O_3 of 1:1. Compared to CuO, CuFe_2O_4 has a good low-temperature oxygen uncoupling property, which is consistent with the DFT calculation results. With the molar ratio CuO: Fe_2O_3 increasing,

there is excessive CuO in the prepared OC. Thus, the temperatures at the peaks of DTG shift to a higher value. However, the mass loss and mass-loss rate of the OC with a molar ratio of 2:1 are biggest. And the oxygen delivery capacity of this OC is 3.65 wt%. This value is lower than copper OC, for example, the oxygen delivery capacity of copper OC with 40 wt% ZrO_2 as binder is 6 wt% [49]. But such oxygen delivery capacity is deemed acceptable for CL reactions. The oxygen transport capacity of OC with a mole ratio of 1:1 is only 1.78 wt%. Based upon the oxygen uncoupling temperature and oxygen transport capacity, the optimal mole ratio of CuO to Fe_2O_3 of 2:1 is selected. And the starting oxygen uncoupling temperature is determined as 749.5 °C, which is lower than the oxygen uncoupling temperature of copper OC (~ 800 °C) [50].

4.2. Reactivity under different oxygen concentrations

The conversion and mass loss rate of OC (with the molar ratio of CuO: $\text{Fe}_2\text{O}_3 = 2:1$) under different local oxygen concentrations is shown in Fig. 7. It can be seen that the starting oxygen uncoupling temperature increased greatly as the local oxygen concentration increases. The reason is that the oxygen uncoupling properties depend on the driving

Fig. 9. Redox behaviour of Cu–Fe composite OC.

Fig. 10. Oxygen uncoupling and oxidation rates of Cu—Fe OC.

force of oxygen uncoupling reaction [49]. When the equilibrium oxygen concentration at a specific temperature is higher than local oxygen concentration around the OC particles, OC begins to release oxygen. Furthermore, the starting temperature at 50.0 vol% O_2 is 1033.5 °C, which increases by 284 °C compared to the value for a N_2 atmosphere. However, at 1033.5 °C, the equilibrium oxygen concentration of Cu-based OC is only 23.2 vol%. This type of OC presents a better low-temperature oxygen uncoupling property. The maximum mass loss rate at 33.3 vol% O_2 is the biggest. When the local oxygen concentration increases further, at 50.0 vol% O_2 , the oxygen uncoupling rate decreases. In CLGOU technology, the oxygen released by OC is consumed immediately by the biochar. Thus, OC always releases oxygen at a relatively low oxygen concentration atmosphere, which allows the oxygen uncoupling process of the OC to proceed. In addition, the gasification temperature can be kept in a low level as a result of the low oxygen uncoupling temperature of the Cu—Fe OC at a low oxygen concentration atmosphere.

4.3. Reactivity under different heating rates

In CLGOU technology, the OC cycles between the air and gasification reactors. Due to the endothermic or exothermic reaction in the reactor, the temperature of OC constantly changes. Thus, it is necessary to get the oxygen uncoupling reactivity data for different heating rates. Fig. 8 shows conversion and mass loss rate of OC under different heating rates. At high heating rates (20, 25 K/min), the starting temperatures increase. Because the thermal hysteresis caused by heat transfer limitations from surface to core in the particles, temperatures at the maximum oxygen uncoupling rates increase with heating rate increasing. Moreover, the oxygen uncoupling rate also increases. It can be explained by the fact that the time needed to reach a high temperature is the shortest with the highest heating rate, and the high temperature is favorable for the oxygen uncoupling reaction. When the heating rates increase further, the increasing trend of oxygen uncoupling rates will become low. The reason is that the driving force of oxygen uncoupling is high enough that the OCs will keep high oxygen uncoupling rates at the higher heating rate conditions.

4.4. Stability of OC

To obtain the stability of OC, redox cycles with N_2 for oxygen uncoupling and air for regeneration were carried out at 900 °C/700 °C oxygen uncoupling and absorbing temperatures. At 900 °C, the oxygen uncoupling rate is high enough (seen from Figs. 6–8). And the gasification conversion and gasification rates of biomass in O_2 -steam

Fig. 11. XRD patterns of the prepared and cycled Cu—Fe OC.

gasification atmosphere is high [25–27]. Fig. 9 illustrates the redox behaviour of Cu—Fe composite OC. This OC exhibits stable performance over 15 consecutive redox cycles. This phenomenon is consistent with the DFT calculation results (the high adsorption energy of CuO onto Fe_2O_3). Moreover, the mass losses in oxygen uncoupling are almost equal to the mass gains in regeneration. The satisfactory oxygen recyclability indicates the OC's suitability for CLGOU.

The oxygen uncoupling and oxidation rates have also been studied and the results are shown in Fig. 10. It can be seen that the oxidation rate is slightly lower than the oxygen uncoupling rate. In industrial CLGOU, these two rates can be balanced by increasing the airflow rate. According to simple order-of-magnitude calculations, the oxygen uncoupling rates are much higher than 0.4 wt%/min for achieving a desirable cracking rate [51–53]. Therefore, the oxygen uncoupling rates of Cu—Fe OC far exceeds the lower bound for usability, and it is a right candidate for CLGOU technology.

The fresh and cycled OC were also characterized for further evaluation its stability. Fig. 11 illustrates XRD patterns of the prepared and cycled samples. The peak positions and relative intensities of the fresh and cycled samples are almost the same. During the redox cycles, the chemical phases keep stable, corresponding to the stable oxygen recyclability of OC. After the composition of CuO and Fe_2O_3 , a new phase of

Fig. 12. SEM-EDX images of the prepared and cycled Cu–Fe OC. (a, b, c – Prepared sample; d, e, f – Cycled sample)

CuFe_2O_4 is formed. Besides CuO , it is another active phase in OC, and the redox reaction can be followed as:

Fig. 12 shows SEM-EDX images of the fresh and cycled samples. The fresh and cycled samples all exhibit porous structures. After cycles, the number of pores has increased due to the consecutive redox reactions, while the surface of OC particle has become smoother due to the crystalline phase migration. No obvious sintering has been observed. The Fe and Cu distributions on the OC surface is similar, which indicates CuFe_2O_4 is the main active phase in OC particles. After cycles, the elements on the surface remain uniformly distributed. The changes of micromorphology indicate the OC have been further active after cycles [50].

Both the specific surface areas of prepared and cycled samples are

very minimal ($0.641 \text{ m}^2\cdot\text{g}^{-1}$ for the prepared sample and $0.735 \text{ m}^2\cdot\text{g}^{-1}$ for the cycled sample). The value has a slight increase after cycles, which is corresponding to the SEM results. Such BET values are typical for OC. The BET values are small, but OC has a high activity. It can be explained by the activity of OC correlates more with internal oxygen transport properties than surface area [54,55]. The crushing strengths for fresh and cycled OC particles are all high (15.7 N for the fresh sample and 14.9 N for the cycled sample). Such crushing strengths are sufficiently high to be used in fluidized bed applications [56].

5. Kinetic analysis

The kinetics of OC plays important roles in determining the required amount of bed material, designing the reactor, and controlling the product distribution in CLGOU [57,58]. To understand the oxygen

Table 3
Different kinetic functions ($G(X)$ and $f(X)$).

Code	Mechanism	Differential $f(X)$	Integral $G(X)$
D_m	Diffusion		
D_1	1-D diffusion	$(1/2)X^{-1}$	X^2
D_2	2-D diffusion	$[-\ln(1-X)]^{-1}$	$X + (1-X)\ln(1-X)$
D_3	3-D diffusion(cylinder)	$(3/2)[(1-X)^{-1/3}-1]^{-1}$	$1-(2/3)X-(1-X)^{2/3}$
D_4	3-D diffusion(sphere)	$(3/2)(1-X)^{2/3}[1-(1-X)^{1/3}]^{-1}$	$[1-(1-X)^{1/3}]^2$
N_m	Nucleation and nuclei growth	$m(1-X)[- \ln(1-X)]^{(m-1)/m}$	$[- \ln(1-X)]^{1/m}$
N_1	$m = 1$	$1-X$	$-\ln(1-X)$
$N_{3/2}$	$m = 3/2$	$(3/2)(1-X)[- \ln(1-X)]^{1/3}$	$[- \ln(1-X)]^{2/3}$
N_2	$m = 2$	$2(1-X)[- \ln(1-X)]^{1/2}$	$[- \ln(1-X)]^{1/2}$
N_3	$m = 3$	$3(1-X)[- \ln(1-X)]^{2/3}$	$[- \ln(1-X)]^{1/3}$
S_m	Shrinking core	$n(1-X)^{(m-1)/m}$	$1-(1-X)^{1/m}$
S_2	$m = 2$	$2(1-X)^{1/2}$	$1-(1-X)^{1/2}$
S_3	$m = 3$	$3(1-X)^{2/3}$	$1-(1-X)^{1/3}$
C_m	Chemical reaction	$(1-X)^m$	$[1-(1-X)^{1-m}]/(1-m)$
C_2	$m = 2$	$(1-X)^2$	$(1-X)^{-1}-1$
C_3	$m = 3$	$(1-X)^3$	$(1/2)[(1-X)^{-2}-1]$

uncoupling characteristic and mechanism, a kinetic model was

Fig. 13. Linear fitting using different kinetic functions.

Table 4
 R^2 , R_{SS} , and y^2 of the different mechanism models.

Models	10 K/min			15 K/min			20 K/min			25 K/min		
	R^2	R_S	y^2	R^2	R_S	y^2	R^2	R_S	y^2	R^2	R_S	y^2
D_m	Diffusion model											
D_1	0.997	0.128	2.088	0.992	0.306	1.119	0.992	0.171	3.235	0.983	0.244	2.910
D_2	0.999	0.049	1.939	0.997	0.141	0.683	0.996	0.096	2.078	0.991	0.165	1.625
D_3	0.999	0.031	1.955	0.998	0.083	0.614	0.998	0.068	1.776	0.994	0.131	1.349
D_4	0.999	0.037	1.970	1.000	0.032	0.627	0.999	0.030	1.773	0.997	0.076	1.361
N_m	Nucleation and nuclei growth model $f(X) = m(1-X)[- \ln(1-X)]^{(m-1)/m}$											
N_1	0.998	0.042	2.326	0.998	0.039	0.779	0.999	0.007	1.363	0.999	0.009	1.195
$N_{1.5}$	0.998	0.019	2.326	0.998	0.017	0.779	0.999	0.003	1.363	0.999	0.004	1.195
N_2	0.997	0.010	2.326	0.998	0.009	0.779	0.999	0.002	1.363	0.999	0.002	1.195
N_3	0.997	0.005	2.326	0.998	0.004	0.779	0.999	0.001	1.363	0.998	0.001	1.195
S_m	Shrinking core model $f(X) = m(1-X)^{(m-1)/m}$											
S_2	0.999	0.007	1.948	0.999	0.015	0.599	0.998	0.014	1.652	0.994	0.028	1.252
S_3	0.999	0.009	1.951	0.999	0.008	0.610	0.999	0.008	1.461	0.997	0.019	1.346
C_m	Chemical reaction model $(1-X)^m$											
C_2	0.984	0.562	3.498	0.979	0.922	1.768	0.989	0.208	2.148	0.990	0.150	2.161
C_3	0.966	2.207	4.825	0.954	4.058	2.879	0.972	0.989	3.454	0.972	0.891	3.174

developed based upon the temperature-programmed experimental data. This model focuses on the oxygen uncoupling process and suits for oxygen uncoupling reaction. The oxygen uncoupling of OC is a typical solid-gas reaction, and the basic kinetic equation is given by [59–61]:

$$\frac{dX}{dT} = (A/\beta) \exp(-E/RT) f(X) \left(1 - \frac{C_{O_2}}{C_{O_2,eq}}\right) \quad (4)$$

where A is pre-exponential factor, s^{-1} ; E is activation energy, $\text{kJ}\cdot\text{mol}^{-1}$; R is universal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$); T is temperature, K ; C_{O_2} is local oxygen concentration, mol/m^3 , $C_{O_2,eq}$ is equilibrium oxygen concentration, mol/m^3 ; $f(X)$ is mechanism function. Table 3 summarizes different kinetic functions ($G(X)$ and $f(X)$).

In Eq. (4), $C_{O_2,eq}$ is given by [62]:

$$C_{O_2,eq} = \frac{101325}{RT} \exp(22 - 2.993 \times 10^4/T - 1.048 \times 10^6/T^2) \quad (5)$$

On TGA, the sample mass in each experiment is small, and the carrier gas flow rate is much higher than the oxygen releasing rate of OC. Thus, the local oxygen concentration is equal to the oxygen concentration in injection gas ($C_{O_2} = 0$).

Integration of Eq. (4) is shown as followed:

Table 5
Dynamics model parameters of Cu–Fe oxygen carrier.

Heating rate (K/min)	10	15	20	25
E_a (kJ/mol)	273.348	246.880	306.031	336.000
A ($\times 10^{-10}$ /s)	0.268	0.017	7.959	19.946

$$G(X) = \int_{T_0}^T (A/\beta) \exp(-E/RT) dT \approx (A/\beta) \int_0^T \exp(-E/RT) dT \quad (6)$$

In this study, the combined Coats-Redfern and Malek method was introduced to obtain dynamic parameters. This method is suitable for multi heating curve, considering the slope and residual of fitting line comprehensively, and has high precision. Eq. (6) is converted as [63]:

$$\ln \left[\frac{G(X)}{T^2} \right] = \ln \left[\int_0^T \left(\frac{A}{\beta} \right) \exp \left(-\frac{E}{RT} \right) dT \right] \approx \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (7)$$

For oxygen uncoupling reaction of OC, the value of $RT/E < 1$, Eq. (7) can be simplified to:

$$\ln \left[\frac{G(X)}{T^2} \right] \approx \ln \left(\frac{AR}{\beta E} \right) - \frac{E}{RT} \quad (8)$$

Linear fitting of Eq. (8) using different kinetic functions (shown in Fig. 13), should yield a high linear correlation coefficient (R^2), while the residuals (R_s) should be small for any suitable mechanism function.

To obtain the most probable mechanism function, Eq. (8) is rewritten as:

$$G(X) = \frac{ART^2}{\beta E} \exp \left(-\frac{E}{RT} \right) \quad (9)$$

Based on the most probable mechanism function, Eq. (10) can be set up:

$$\frac{f(X)G(X)}{f(X_{0.5})G(X_{0.5})} = \frac{T^2}{T_{0.5}^2} \frac{dX/dT}{(dX/dT)_{0.5}} \quad (10)$$

In Eq. (10), the left hand side is a model value, whereas the right hand side is an experimentally determined value, the residuals (y^2) of model and experimental values are obtained. Table 4 shows R^2 , R_{SS} , and y^2 of the different mechanism models for the oxygen uncoupling of Cu–Fe OC.

Comprehensive considerations of the highest R^2 and the smallest R_{SS} , and y^2 , the most probable mechanism function of shrinking core model ($m = 3$) has been determined. The oxygen uncoupling rate is controlled by the chemical reaction. During oxygen uncoupling process, the reaction layer penetrates into the core product from the surface of the particles and retains the morphology similar to the original particles. Using the slopes ($-E/R$) and intercepts ($\ln(AR/\beta E)$) of the fitting lines in Fig. 13 (b), the dynamic parameters are obtained, which are shown in Table 5. As shown in Fig. 8(a), the smooth solid curves are the model results. It can be seen that the established model describes the experimental data well, especially when the conversion of OC is lower than 95%.

6. Conclusions

Aiming to increase the gasification rate of CLG, a Cu–Fe OC with oxygen uncoupling capability was proposed to be used in CLGOU. The oxygen uncoupling reactivity and stability of OC have been computationally and experimentally investigated. In addition, oxygen uncoupling kinetic model was developed.

1) DFT analysis shows that a chemical reaction occurs after Cu_4O_4 cluster adsorption onto α - Fe_2O_3 (0 0 1) surface. Extension of bond length and transfer of charge indicate the composite oxide has been activated. The calculated binding energy is high (−6.14 eV) and the

sintering resistance characteristic of Cu–Fe composite OC should be high.

- 2) An optimal molar ratio of 2:1 of CuO to Fe_2O_3 is used for the preparation of OC ((by mechanical mixing) and oxygen delivery capacity of the OC is determined at 3.65 wt%. This OC presents a good low-temperature oxygen uncoupling property, and the starting uncoupling temperature was found to be 749.5 °C.
- 3) The starting uncoupling temperature increased significantly with an increase in local oxygen concentration. The chemical and physical characteristics kept stable over cycles. And the oxygen uncoupling rates are much higher than the lower bound (0.4 wt%/min) for cracking. The most probable mechanism function was found to be a shrinking core model ($m = 3$) with which the oxygen uncoupling reaction kinetics can be described well. The investigated Cu–Fe composite OC is promising for CLGOU.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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