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# Self-assembly template combustion synthesis of a core–shell CuO@TiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> hierarchical structure as an oxygen carrier for the chemical-looping processes

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# ABSTRACT

Chemical looping combustion (CLC) and chemical looping with oxygen uncoupling (CLOU) are the most promising technologies for capture of CO<sub>2</sub> at a low cost. CLC and CLOU involve cyclic reduction and oxidation of a solid oxygen carrier (OC) to transfer active oxygen from air to carbon-based fuels for combustion with the inherent feature of isolating  $CO_2$ . One key issue with these technologies is to manufacture a high-performance, economical and practical OC material. In this paper, we propose a self-assembly template combustion synthesis (SATCS) method for preparing a hierarchical structure copper-based OC, Cu-rich, Al<sub>2</sub>O<sub>3</sub>-supported and TiO<sub>2</sub>-stabilized in a core-shell microarchitecture. The selection of raw materials and the rational design of OCs are based on the density functional theory (DFT) calculations and the classical Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, respectively. The spontaneous aggregation between  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> microparticles ( $\mu$ m-Al<sub>2</sub>O<sub>3</sub>) and rutile TiO<sub>2</sub> nanoparticles (nm-TiO<sub>2</sub>) is driven by the van der Waals attractive and electrostatic attractive forces to form core(Al<sub>2</sub>O<sub>3</sub>)-shell(TiO<sub>2</sub>) hard templates in the wet precursor containing copper nitrate and urea. Upon calcination of the dried precursor in air, fewer nitrogen oxides (NO<sub>x</sub>) are released, demonstrating an environment-friendly fabrication process, whereby a highly dispersed and high-loading Cu-based crystalline layer is deposited on the nanostructured shell. A representative CuO@TiO2-Al2O3 OC (17.5 wt% Al2O3, 5 wt% TiO2) possesses hierarchical porosity and an interconnected framework and exhibits excellent performance of the reactivity, stability, oxygen release/uptake capacity and mechanical strength in the high-temperature redox cycles. The proper addition of TiO<sub>2</sub> nanoparticles is effective in preventing the formation of copper aluminates (CuAl<sub>2</sub>O<sub>4</sub> and CuAlO<sub>2</sub>) and inhibiting the sintering of active component grain. In addition, the rational design method and novel synthesis technique allow a mass production of various metal oxide composites used for chemical looping processes with CO<sub>2</sub> capture and clean utilization of energy.

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# 1. Introduction

The chemical looping (CL) technique is an attractive solution for concentration and separation of CO<sub>2</sub> from fossil fuels with a low economic cost and energy penalty. Several variants of chemical looping technologies are available, e.g., chemical looping combustion (CLC) [1], chemical looping with oxygen uncoupling (CLOU) [2], chemical looping air separation (CLAS) [3], chemical looping reforming (CLR) [1], and chemical looping hydrogen production (CLH) [4]. Typically, in a CL system, two reactors, a fuel reactor (FR) and an air reactor (AR), are interconnected while isolated from each other in a reaction atmosphere. Oxygen carrier (OC) particles

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circulate to carry active oxygen from air to carbonaceous fuel between the AR and the FR [5]. Thus, the CL processes are involved with a cyclic reduction–oxidation reaction, and the OC particles are required to demonstrate high reactivity, thermal stability, mechanical strength, fluidizability, environmental friendliness, low cost, and resistance to agglomeration and sintering.

Copper oxide has received a great deal of attention as an efficient OC because it has some advantageous characteristics of high reactivity, high oxygen transport capacity, suitable equilibrium partial pressure of oxygen at temperatures of interest for combustion (800–1000 °C), stable recyclability of oxygen release and uptake, moderate price, and being exothermic for fuel combustion in the FR [1,6]. However, CuO suffers from a tendency toward sintering and agglomeration upon full reduction, forming metallic copper with a rather low melting temperature (1083 °C). Lower

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# Nomenclature

Latin syı	nbols
A <sub>H</sub>	Hamaker constant [J]
С	ion concentration [mol L <sup>-1</sup> ]
е	elementary charge 1.6 $ imes$ 10 $^{-19}$ C
f	volume fraction of support
Finteract	interaction force between support and CuO [J $m^{-2}$ ]
$k_{\rm B}$	Boltzmann constant, $1.38 imes 10^{-23}\mathrm{JK^{-1}}$
Kw	ion-product constant of water
1	distance between the surfaces of two interacting parti-
	cles [m]
Μ	solid state diffusion strength
т	mass of OC [kg]
$M_0$	amount of active oxygen in unreacted OC [mol]
$m_{\rm bed}$	mass of OC needed in reactor [kg $MW_{th}^{-1}$ ]
$m_{\rm ox}$	fully oxidized state mass of OC [kg]
iπ <sub>0</sub>	stoichiometric mass flow of oxygen necessary [kg $s^{-1}$ ]
$m_{\rm red}$	fully reduced state mass of OC [kg]
$\dot{m}_{ m sol}$	oxygen carrier recirculation rate [kg MW <sup><math>-1</math></sup> s <sup><math>-1</math></sup> )
$n_{\rm in,CH4}$	molar flow of dry $CH_4$ entering reactor [mol s <sup>-1</sup> ]
р	partial pressure of gas [Pa]
$P_{tot}$	total pressure of gases [Pa]
R	grain radius of CuO [m]
r	radius of support particle [m]
Ro	theoretical oxygen ratio of OC in CLC
$R_{AO}$	actual oxygen transport capacity of OC

operating temperatures (800–850 °C) in the FR and/or AR are advantageous for resistance to sintering, agglomeration and defluidization but disadvantageous for fast reaction kinetics and high energy utilization efficiency [7,8]. Usually, the active component CuO is supported by different inert materials of, e.g., ZrO<sub>2</sub>, MgAl<sub>2</sub>O<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, MgO, TiO<sub>2</sub>, and sepiolite to withstand a higher temperature (such as 900–1000 °C) [2,7,9–14]. Several Cu-based OCs have been developed using different supports and preparation methods. Among various supports for the CuO oxygen carriers, Al<sub>2</sub>O<sub>3</sub> has received considerable attention for increasing the temperature resistance and durability of Cu-based OCs [9,14–16], owing to its high melting point, high mechanical strength, and low cost.

The support is known to have a great influence on the behavior of the OCs. In the case of  $Al_2O_3$  as a support, the  $CuAl_2O_4$  spinel is invariably formed during OC preparation at high temperatures (approximately 900–1200 °C) by the interaction between CuO and Al<sub>2</sub>O<sub>3</sub>, resulting in the partial loss of CuO [7,16]. Although CuAl<sub>2</sub>O<sub>4</sub> is fully reducible and can also release gaseous O<sub>2</sub> under lower oxygen partial pressure and high-temperature conditions, the reaction rate is much lower than the reaction rate of CuO [17]. This interaction needs to be avoided to retain CuO as an active phase for CLOU, however, but the interaction seems to be difficult to inhibit in our previous investigations [18,19]. Using copper nitrate and aluminum isopropoxide as raw materials, CuO/CuAl<sub>2</sub>O<sub>4</sub> rather than the expected CuO/Al<sub>2</sub>O<sub>3</sub> was produced by calcining the Cu(OH)<sub>2</sub>/ $\gamma$ -AlOOH sol-gel precursor at 1000 °C for 10 h [18]. CuO/CuAl<sub>2</sub>O<sub>4</sub> OC (CuO, 60 wt%:CuAl<sub>2</sub>O<sub>4</sub>, 40 wt%) was able to release and absorb gaseous O2 repeatedly at combustion temperatures (800-1000 °C) without agglomeration and sintering and could attain nearly complete conversion of coal in the FR. However, there was actually 17.5 wt% active CuO loss because full CuAl<sub>2</sub>O<sub>4</sub> was not involved with redox during the CL process. Even earlier, Chuang et al. [7] also found that there was an interaction between  $Al_2O_3$  and CuO to form  $CuAl_2O_4$  under high-temperature conditions. Recently, we found that once the

	11	
	R <sub>ij</sub>	center-to-center separation between particle <i>i</i> and <i>j</i> [m]
	R <sub>max</sub>	maximum radius of CuO grain during growth [m]
	R <sub>O</sub>	theoretical oxygen transport capacity of OC in CLOU
	ro	oxygen transport rate of OC
	t	time [s]
	Т	temperature [K]
	$V_{\rm edl}$	electric double layer repulsive/attractive energy [J]
-	V <sub>T</sub>	DLVO total interaction energy [J]
	V <sub>vdw</sub>	van der Waals attractive energy [J]
	Χ	OC conversion with methane reduction in CLC
	X <sub>max</sub>	maximum conversion of OC in cyclic TG tests
	X <sub>ox</sub>	oxidation conversions of OC
	$X_{\rm red}$	reduction conversions of OC
	Y	dimensionless effective surface potential
	Ζ	ion valence value
	Greek svi	nbols
	α	geometry shape factor
	ν	specific surface energy $[I m^{-2}]$
	7 80	permittivity in vacuum $[C^2 I^{-1} m^{-1}]$
	Er	relative dielectric constant of medium
	κ	reciprocal of double layer thickness $[m^{-1}]$
	$\Psi_i$	surface potential of particle <i>i</i> [V]
	$\omega$	mass-based conversion of OC

radius of particle *i* [m]

sol-gel-derived-CuO/CuAl<sub>2</sub>O<sub>4</sub> was fully reduced to metal Cu and Al<sub>2</sub>O<sub>3</sub> by carrying out a deep reduction with H<sub>2</sub>, CuAl<sub>2</sub>O<sub>4</sub> would not be generated again in subsequent redox reactions [20]. This phenomenon may be attributed to the physical restructuring of OC particles after deep reduction. Although CuO can be more fully utilized in this way, there is a higher risk of agglomeration and sintering when high metal Cu content appears.

It is thus necessary to minimize the interaction between the support and the active component during the preparation process. Imtiaz et al. [21] employed the co-precipitation technique to synthesize Cu-based and Al<sub>2</sub>O<sub>3</sub>-stabilized OCs using KOH as the precipitating agent, and the OCs were calcined and evaluated at 800 °C. The residual K<sup>+</sup> ions can inhibit CuAl<sub>2</sub>O<sub>4</sub> formation, but the inhibiting effect was not examined at higher calcination or redox temperatures (e.g., 900–1000 °C). Similarly, Song et al. [22] discovered that the presence of Na<sup>+</sup> ions was effective in inhibiting the formation of copper aluminates (CuAl<sub>2</sub>O<sub>4</sub> or CuAlO<sub>2</sub>) and stabilizing the copper phase in an amorphous support over multiple redox cycles. However, the Cu-Al OC with a high loading of CuO of 82.5 wt% may agglomerate in the CO-fueled CLC when cycled at temperatures above 900 °C and demonstrated a considerable attrition rate. Other commonly-used supports, e.g., TiO<sub>2</sub>, do not react with CuO. However, the resulting Cu-based OCs demonstrated a low mechanical strength and an agglomeration problem [11,23]. As for the other supports (MgAl<sub>2</sub>O<sub>4</sub> and ZrO<sub>2</sub>), the evaluations of the OCs with respect to price and mechanical stability are not satisfactory [10,11,24].

To summarize, a single material as a support has its limitations within chemical stability, mechanical strength and temperature resistance. However, a composite support is combined from two or more constituent materials with different physical or chemical properties and may produce some substantial complementary characteristics different from the individual components to improve the comprehensive performance of Cu-based OCs. Recently, Adánez-Rubio et al. [10] examined the Cu-based OC materials that were manufactured by spray-drying from water-based slurries of a mixture of CuO with MgAl<sub>2</sub>O<sub>4</sub>/TiO<sub>2</sub>, MgAl<sub>2</sub>O<sub>4</sub>/SiO<sub>2</sub>, and TiO<sub>2</sub>/SiO<sub>2</sub> in terms of their CLOU effect. Each of the given OCs could not simultaneously satisfy the comprehensive performance requirements including but not limited to high mechanical stability, low attrition rate and good reactivity. Therefore, extensive efforts are required to develop an OC material with all aspects of performance. On the one hand, it is important to understand the interaction between the active phase and the support phase for screening appropriate raw materials. On the other hand, it is necessary to pay attention to the synthetic route for designing the microstructure of OC particles. In this work, according to previous experimental research and theoretical calculations, we selected Al<sub>2</sub>O<sub>3</sub> as the main support and TiO<sub>2</sub> as the minor support of the CuO component and designed a novel CuO@TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> OC material based on the self-assembly between TiO<sub>2</sub> nanoparticles (nm-TiO2) and  $Al_2O_3$  microparticles ( $\mu$ m- $Al_2O_3$ ), where nm-TiO<sub>2</sub> particles were coated on the surface of µm-Al<sub>2</sub>O<sub>3</sub> particles to inhibit the interaction of active phase CuO with the main support Al<sub>2</sub>O<sub>3</sub>.

The OCs were usually synthesized on an experimental scale utilizing a well-rounded chemical or physical method. The alternative methods for OC preparation included sol-gel, impregnation, co-precipitation, hydrothermal synthesis, low heating solid state reaction, freeze granulation, combustion synthesis, mechanical mixing, etc. [1,7,11,18,25–27]. The liquid preparation methods (e.g., sol-gel method), which usually use a nitrate solution of the target metal oxides as precursors, can attain a high purity, accurate stoichiometry of the products, controllable microstructure, and homogeneous mixing of components almost at the molecular level, yielding a high degree of dispersion and high loading of active metal oxide in the support after calcination. However, the liquid preparation methods usually suffer from a long preparation period and complex preparation processes that are almost involved in drying and granulation. In addition, the environmental influence should be paid close attention in the productive processes of OCs. Typically, nitric oxide  $(NO_x)$  emissions result from the decomposition of nitrates during OC preparation processes. We proposed a sol-gel combustion synthesis (SGCS) method for the preparation of  $Fe_2O_3/Al_2O_3$  and  $CuFe_2O_4$  OC particles [28]. The self-propagating high temperature synthesis (SHS) relies on the combustion reaction between oxidizer (metal nitrates) and fuel (urea, citric acid or glycine, etc.) [29]. The SGCS method combines the advantages of sol-gel and SHS, including rapidity and simplicity, low energy consumption, molecular mixing of the precursors, and good resistance to sintering [30]. The SGCS method has the potential to reduce or even eliminate the  $NO_x$  emissions from OC synthesis. In this paper, we further develop a novel self-assembly template combustion synthesis (SATCS) method based on the SGCS method for preparation of CuO@TiO2-Al2O3 OC particles. Compared with conventional combustion synthesis (e.g., self-propagating high-temperature synthesis (SHS), solution combustion synthesis (SCS) [31]), the proposed SATCS involves a particular process in which self-assembly of support particles is driven by van der Waals and Coulombic interactions to form orderly core-shell structures as hard templates for efficiently dispersing and supporting active component.

## 2. Theoretical insights into OC design

# 2.1. Density functional theory (DFT) investigations for CuO-support interactions

A fundamental understanding of the microcosmic mechanisms of oxygen release and the interactions of different phases in OC particles could help rationalize the design of high performance OCs. In our recent papers [17,32], the periodical density functional

theory (DFT) calculations were used to investigate the effects of different supports (TiO<sub>2</sub>, ZrO<sub>2</sub>, MgAl<sub>2</sub>O<sub>4</sub>, and CuAl<sub>2</sub>O<sub>4</sub>) on the performance of Cu-based OCs (several popular support materials). The aim of DFT calculations was to clarify some basic factors in determining the OC reactivity and sintering resistance. A lower energy barrier for the oxygen release process favors the OC reactivity, and a higher adsorption energy between support and CuO benefits the OC sintering resistance. The corresponding energy barriers for oxygen release and adsorption energies of  $CuO/TiO_2$  and  $CuO/CuAl_2O_4$  were presented in Fig. 1. The oxygen release proceeds in two steps: (i) the formation of an O<sub>2</sub> complex on the CuO nanocluster; and (ii) the desorption of molecular O<sub>2</sub> to the gas phase. The energy barriers for CuO/TiO<sub>2</sub> in the two steps are always lower than the energy barriers of CuO/CuAl<sub>2</sub>O<sub>4</sub> in the whole oxygen release process, but the adsorption energy of CuO/TiO<sub>2</sub> is relatively weak. In this context, TiO<sub>2</sub> as a support benefits the reactivity of CuO. However, TiO<sub>2</sub> is not particularly satisfactory at sintering resistance for OCs due to a lower adsorption energy (absolute value) and melting point. Generally, it is necessary to achieve a compromise between the oxygen release energy barrier and the adsorption energy of CuO on the support to attain favorable performance of Cu-based OCs. So we designed a composite support combining TiO<sub>2</sub> with Al<sub>2</sub>O<sub>3</sub> via a self-assembly template combustion synthesis in which TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> serve as an enhancer for the reactivity and sintering resistance of Cu-based OCs.

#### 2.2. Zener pinning theory for analyzing CuO sintering

Sintering of OC particles is essentially solid-state diffusion driven by the decrease of grain surface energy, and its kinetics depends not only on physicochemical properties (e.g., specific surface energy, adsorption energy, *etc.*) of component materials but also on the particle size and content of support. The Zener pinning theory [27,33] provides a route to understand the CuO grain radius growth kinetics, as follows [33]:

$$\frac{dR}{dt} = \alpha M \left[ \frac{2\gamma}{R} - \left( \frac{3f}{2r} \right) F_{\text{interact}} \right]$$
(1)

where *R* is the grain radius of CuO [m],  $\alpha$  is the geometry shape factor, *M* is the solid state diffusion strength,  $\gamma$  is the specific surface energy of CuO [J m<sup>-2</sup>], *f* is the volume fraction of support, *r* is the radius of support particles [m], *F*<sub>interact</sub> is the interaction force between support and CuO, simplified as the specific surface energy of support material [J m<sup>-2</sup>]. The performance and characteristics of OCs can be interpreted qualitatively using Eq. (1). When the growth rate is equal to 0 (i.e., dR/dt = 0, termination of growth), the maximum radius of the CuO grain is attained and can be deduced as

$$R_{\rm max} = \frac{4}{3} \left( \frac{\gamma}{F_{\rm interact}} \right) \left( \frac{r}{\bar{f}} \right) \tag{2}$$

Generally, there is not much difference in surface energy between CuO and some popular support materials, namely,  $\gamma/F_{\text{interact}} \approx 1$  (e.g., for CuO/TiO<sub>2</sub>,  $\gamma/F_{\text{interact}} = 0.86$  [27,34]; for CuO/CuAl<sub>2</sub>O<sub>4</sub>,  $\gamma/F_{\text{interact}} = 0.53$  [17,34]), whereas the variation of support particle size (r) and fraction (f) can effectively influence the maximum radius of the CuO grain. Obviously, the smaller support particle size (r) can inhibit grain growth better in a high-loading active component. It is expected that nanolevel support particles (TiO<sub>2</sub> nanoparticles in this paper) possess an outstanding effect for preventing active component sintering.

# 2.3. Particle dynamics in aqueous suspensions of precursors

Liquid-phase preparation methods have irreplaceable advantages in raw material mixtures and formation of precursors.



**Fig. 1.** Potential energy profiles of the CuO oxygen release process for CuO/TiO<sub>2</sub> and CuO/CuAl<sub>2</sub>O<sub>4</sub>, corresponding energy barriers of O<sub>2</sub> formation and of O<sub>2</sub> desorption. The top left inset shows the adsorption energies between the CuO cluster and two support planes (for modulus, CuO/TiO<sub>2</sub> < CuO/CuAl<sub>2</sub>O<sub>4</sub>).

However, a mediocre hybrid of raw materials is not infeasible because it is necessary to avoid direct contact of CuO and Al<sub>2</sub>O<sub>3</sub> in OC particles, and particle coating is supposed to be a desirable way to attain this aim. Core-shell composite particles, bigger Al<sub>2</sub>O<sub>3</sub> particles coated with smaller TiO<sub>2</sub> particles (here, Al<sub>2</sub>O<sub>3</sub> microparticles and TiO<sub>2</sub> nanoparticles are considered) can be achieved by enhancing hetero-coagulation in the TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> binary dispersions. The ability to control particle stability and assembly is crucial for the effective processing of precursor suspensions. The well-known Derjaguin-Landau-Verwey-Overbeek (DLVO) theory is most commonly used to describe the thermodynamic interactions between two particles in a suspension [35,36]. The DLVO total interaction energy  $(V_T)$  is the sum of the van der Waals attractive (V<sub>vdw</sub>) and electric double layer repulsive/attractive  $(V_{edl})$  potentials that exist between particles as they undergo Brownian motion.

$$V_{\rm T} = V_{\rm vdw} + V_{\rm edl} \tag{3}$$

The van der Waals attractive energy and electrical double layer repulsive/attractive energy are expressed as [37]:

$$V_{\rm vdw} = -\frac{A_{\rm H}}{6} \left[ \frac{2r_i r_j}{R_{ij}^2 - (r_i + r_j)^2} + \frac{2r_i r_j}{R_{ij}^2 - (r_i - r_j)^2} + \ln \frac{R_{ij}^2 - (r_i + r_j)^2}{R_{ij}^2 - (r_i - r_j)^2} \right]$$
(4)

$$V_{\text{edl}} = \begin{cases} 4\pi\varepsilon_{\text{r}}\varepsilon_{0}\psi_{i}\psi_{j}\frac{r_{i}r_{j}}{r_{i}+r_{j}}\ln[1+\exp(-\kappa l)], & \kappa r \ge 5\\ 4\pi\varepsilon_{\text{r}}\varepsilon_{0}r_{i}r_{j}Y_{i}Y_{j}\left(\frac{k_{\text{B}}T}{e}\right)^{2}\frac{\exp(-\kappa l)}{R_{ij}}, & \kappa r < 5 \end{cases}$$
(5)

where  $A_{\rm H}$  is the Hamaker constant [J],  $r_i$  and  $r_j$  are the radii of particle *i* and *j*, respectively [m],  $R_{ij}$  is the center-to-center particle separation [m], *l* is the distance between the surfaces of two interacting particles [m],  $\kappa$  is the reciprocal of the thickness of the double layer [m<sup>-1</sup>].  $\varepsilon_{\rm r}$  is the relative dielectric constant of the medium and  $\varepsilon_0$  is the permittivity in vacuum,  $\Psi$  is the surface potential [V], estimated by the zeta potential of the charged particles, and Y is the dimensionless effective surface potential, Y = 4 tanh[ $e\Psi/(4k_{\rm B}T)$ ].

The  $Al_2O_3$  and  $TiO_2$  binary particle suspension can involve three different types of interactions:  $Al_2O_3$ – $Al_2O_3$  (A–A),  $Al_2O_3$ – $TiO_2$ (A–T), and  $TiO_2$ – $TiO_2$  (T–T). Based on the DLVO theory, it is possible to reach stabilization for like particles (i.e., A–A or T–T) due to like-charged repulsion, whereas charge heterogeneity for unlike particles can promote fast coagulation of A–T. The greater the difference between the isoelectric points (IEPs) of particles, the better coating effect can be achieved in aqueous suspension [38]. After testing a variety of TiO<sub>2</sub> materials, we found that flame-synthesized rutile TiO<sub>2</sub> nanoparticles (nm-TiO<sub>2</sub>) have resulted in a greater difference of IEP values from the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> microparticles (µm-Al<sub>2</sub>O<sub>3</sub>). Figure 2 shows the zeta potential as a function of pH for µm-Al<sub>2</sub>O<sub>3</sub> and nm-TiO<sub>2</sub>, measured using a micro-electrophoresis apparatus (Powereach JS94H, Shanghai Zhongchen Digital Technical Apparatus Co., Ltd, China), where the IEP values of nm-TiO<sub>2</sub> and µm-Al<sub>2</sub>O<sub>3</sub> are approximately 3.4 and 9.0, respectively. The zeta potential of the particle was correlated with the pH level and decreased with increasing pH. At pH 6, the biggest potential difference with opposite charges appeared.

In the current experiments, the total interaction energy  $(V_{\rm T})$ under different pH conditions was calculated based on the expressions in Eqs. (3)–(5), using parameters described in Table 1. For unlike particles (A–T), the van der Waals force and electrostatic force together are responsible for aggregating owing to simultaneous attraction, and particles have a maximum net attractive energy at pH = 6. On the other side, agglomeration between like particles (A-A or T-T) is most significant near the IEP as the electrical double layer diminishes, and the attractive energy due to van der Waals forces becomes dominant [37]. As the suspension pH deviates from the IEP, the electrical double layer thickness increases as does the surface charge (either positive or negative) and thus greater repulsion and smaller agglomerates are expected for like particles. The above behavior was illustrated in Fig. 3. We examined the microstructure (TEM images) of steady agglomerates from the  $Al_2O_3$ -TiO<sub>2</sub> suspension of sample B at pH = 5 and 6, respectively, as shown in Fig. 4. Here we have to show smaller Al<sub>2</sub>O<sub>3</sub> particles and therefore possess clearer TEM micrographs because electron beams are difficult to pass through thick samples in a TEM. The TiO<sub>2</sub> layer (green-line profiles) was thinner and uneven on the Al<sub>2</sub>O<sub>3</sub> core (red-line profiles), and there were obvious aggregations for nm-TiO<sub>2</sub> at pH = 5 (Fig. 4a), whereas the  $Al_2O_3$  core was coated with a high coverage density of the nm-TiO<sub>2</sub> cluster spreading outward from the core surface to the shell external boundary at pH = 6 (Fig. 4b). The experimental observations were consistent with the DLVO calculations of particle interactions, indicating that the pH level has significant effects on the formation of the core(Al<sub>2</sub>O<sub>3</sub>)-shell(TiO<sub>2</sub>) structure, so the electric double layer force is a critical driver of the self-assembly. Consequently, when the pH level of the dispersions was adjusted to 6, the interaction between particles achieved an optimal coating effect (enhancing



Fig. 2. Zeta potential of  $\mu$ m-Al<sub>2</sub>O<sub>3</sub> and nm-TiO<sub>2</sub> as a function of pH levels. The vertical bars represent a standard deviation of five repeated measurements.

#### Table 1

Parameters used in the DLVO calculations.

	Particle radius <sup>a</sup>	Hamaker constant A <sub>H</sub> in water (J) [36,39]
Al <sub>2</sub> O <sub>3</sub> TiO <sub>2</sub> Al <sub>2</sub> O <sub>2</sub> -TiO <sub>2</sub>	8.7 μm 22.4 nm -	$\begin{array}{l} 4.57\times 10^{-20}\\ 3.75\times 10^{-20}\\ 4.14\times 10^{-20}\end{array}$

<sup>a</sup> Geometric mean radius of particle population with an approximate lognormal distribution.



**Fig. 3.** Calculated interaction potential energy of particles as a function of pH levels at the suspension. At temperature 353 K, the ion-product constant of water is  $K_W = [H^+] \cdot [OH^-] = 2.36 \times 10^{-13}$ ; the relative dielectric constant of water is  $\varepsilon_r = 81.6$ ; the permittivity is  $\varepsilon_0 = 8.85 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$  in vacuum;  $\kappa = 6.643 \times 10^7 (\sum_n C_n Z_n^2)^{1/2}$  where  $C_n$  is the concentration of ion *n*, and  $Z_n$  is its valence value; Boltzmann constant  $k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$ . The center-to-center particle separation  $R_{ij} = 34.1 \, \mu\text{m} (\text{A}-\text{A})$ , 141.5 nm (T–T) and 8.8  $\mu$ m (A–T) based on average particle distance in a suspension.

hetero-coagulation and diminishing homo-coagulation) to quickly and efficiently form core-shell structured templates.

# 3. Experimental

# 3.1. Synthesis of Cu-based OCs

In this study, we synthesized four types of Cu-based OC materials (marked as A, B, C and D, 100 g of each) with same content of CuO (77.5 wt%), and different contents of TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, and details of the samples were shown in Table 2. Commercial  $\mu$ m-Al<sub>2</sub>O<sub>3</sub> particles were selected as the main component of the support, whereas nm-TiO<sub>2</sub> particles were deposited on the surface of  $\mu$ m-Al<sub>2</sub>O<sub>3</sub> by the electrostatic self-assembly in precursors to modify and stabilize the support. A schematic sketch of the individual synthesis steps was shown in Fig. 5, and detailed descriptions were given below.

(1) The nm-TiO<sub>2</sub> was prepared using flame synthesis technology – a single step, a continuous and scalable process. The gas flame synthesis facility was designed, as shown in Fig. 6, in which a four-concentric-tube burner was fed with TiCl<sub>4</sub> (vapor) and N<sub>2</sub> (as a dilute gas and carrier gas), CH<sub>4</sub> (fuel), O<sub>2</sub> (oxidizer), and N<sub>2</sub> (sheath gas), from the outside to the center. More detailed operating conditions and experimental data about the flame synthesis are available in reference [40]. The co-flow diffusion CH<sub>4</sub> flame established a controllable and stable high-temperature field that provides the energy needed for the nanoparticle synthesis, including the



Fig. 4. TEM micrographs of the  $Al_2O_3$ -Ti $O_2$  agglomerates from the suspension at (a) pH = 5; (b) pH = 6.

oxidation of the TiCl<sub>4</sub>, the crystal transition and morphology evolution of particles. The nm-TiO<sub>2</sub> with complete rutile phase (see Fig. 7), and a good crystalline nature within the size range 10-50 nm (its morphology as shown in Fig. 8) can be obtained by regulating gas flow rates.

- (2) The calculated amount (according to the expected mass ratio with respect to Table 2) of μm-Al<sub>2</sub>O<sub>3</sub> (particle size 1–75 μm, Sinopharm, AR level) and nm-TiO<sub>2</sub> powder was uniformly dispersed in 300 mL hot water (80 °C, water bath heating). After stirring one hour, the suspension pH level was readjusted to 6 by adding dilute nitric acid or ammonia solution.
- (3) 97.5 g of urea  $(CO(NH_2)_2 \text{ crystals}, \text{Sinopharm}, \text{AR level})$  was added to the slurry to stabilize the templates by increasing the steric hindrance of the dispersion system. In addition, the urea was used as a fuel burned with copper nitrate in the subsequent combustion synthesis process.
- (4) 235.4 g copper nitrate trihydrate crystals (Cu(NO<sub>3</sub>)<sub>2</sub> · 3H<sub>2</sub>O, Sinopharm, AR level) was added to the template slurry under the conditions of full stirring. Cupric ions (Cu<sup>2+</sup>) were uniformly dispersed in the system, forming stable complex ions {Cu[CO(NH<sub>2</sub>)<sub>2</sub>]<sub>2</sub>}<sup>2+</sup> with urea molecules, capable of avoiding crystallization segregation of Cu<sup>2+</sup> during the subsequent drying process.

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Table 2					
Oxygen	carriers	prepared	in	this	work.

Sample	Raw materials	Raw materials (g)					Support phase
	μm-Al <sub>2</sub> O <sub>3</sub>	nm-TiO <sub>2</sub>	$CO(NH_2)_2$	$Cu(NO_3)_2\cdot 3H_2O$	$Al(C_3H_7O)_3$		
А	22.5	0	97.5	235.4	-	CuO	$CuAl_2O_4 - Al_2O_3$
В	17.5	5.0	97.5	235.4	-		TiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>
С	12.5	10.0	97.5	235.4	-		TiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>
D	0	22.5	97.5	235.4	-		TiO <sub>2</sub>
E (sol-gel)	-	-	-	235.4	45.0		$CuAl_2O_4$



Fig. 5. Schematic of the different steps of synthesis of Cu-based OCs using the SATCS method. A series of simplified physical models for the structure fabrication was shown in the bottom row.



Fig. 6. Schematic diagram of the flame synthesis of rutile nm-TiO<sub>2</sub> (product nm-TiO<sub>2</sub> as an additive to self-assembly template combustion synthesis OCs).



Fig. 7. XRD pattern of flame-synthesized nm-TiO<sub>2</sub>.

- (5) The wet precursor was dried in an electrically heated drying oven (80 °C for 24 h), and then the dried precursor was transferred into a temperature-programmed muffle furnace and ignited at 200 °C in air. The combustion synthesis method can utilize the inner heat source to accelerate the drying and evolution from pyrolysis and achieve a high calcination temperature. The as-burned precursor proceeded to be calcined in the muffle furnace at 950 °C for 2 h. Then, the temperature dropped to room temperature by the natural cooling.
- (6) Finally, the conglomeration was ground into particles and sieved to yield the OC product in the size range of 0.125– 0.180 mm.

In addition, a sol–gel-derived CuO/CuAl<sub>2</sub>O<sub>4</sub> OC (i.e., sample E as shown in Table 2) with the same size range was prepared according to our previous work [18], compared with the self-assembly template combustion synthesis OCs in a contrastive investigation.

#### 3.2. Characterization techniques

The mechanical strength of some fresh and used samples, determined using a digital force gauge (Shimpo, FGJ-5), was taken as the average value of 30 measurements of the force needed to crush an OC particle. The attrition rates of fresh OCs were determined in a standard abrasion tester (a stainless steel cylinder of length

14.5 cm and diameter 12.0 cm, with a 1.5 cm baffle), and rotated on a ball-mill roller for 50 min at a rate of 10 rpm. The specific surface area and specific pore volume of OCs were characterized in a physisorption apparatus (Micromeritics ASAP-2020) by multipoint nitrogen adsorption at 77 K using the Brunauer-Emmett-Teller (BET) and the Barrett-Joyner-Halenda (BJH) methods, respectively. The determination of particle size distribution (PSD) was made with a laser diffraction particle size analyzer (Malvern Mastersizer 2000) that allows the size to range from 0.02 to 2000 µm. The crystalline phase species of the fresh and used OCs was determined using a powder X-ray diffractometer (XRD, Shimadzu X'Pert Pro) using Cu K $\alpha$  radiation ( $\lambda$  = 0.1542 nm, the accelerating voltage of 40 kV and the tube current of 40 mA) in a 2  $\theta$  angular range of 20–90°. The microstructure of OC samples was analyzed in a field emission scanning electron microscope (FSEM, FEI Nova Nano SEM 450) coupled with an energy-dispersive X-ray spectrometer (EDS, Oxford X-Max 50). Some samples were also observed in a transmission electron microscope (TEM, FEI Tecnai G2 20). To analyze the internal section of the OC particles and the morphology of the inert support, we designed two methods to prepare microscopic samples: (1) OC particles were embedded in epoxy resin and polished to obtain the cross-section of particles; (2) OC particles were immersed in an ammonia-ammonium carbonate solution (ammonia with a concentration of 2.8 mol  $L^{-1}$ ,  $[NH_4^+]$ : $[NH_3] = 0.6$ ), in which the active species (CuO) was dissolved to obtain the framework of the inert support). The internal microstructures of the particles and element distribution in the exposed cross-section were characterized using BSE (backscattered electron) images and EDS maps, and the skeletons of the dissolved CuO particles were used to analyze the structure of TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> composite support using SE (secondary electron) images.

# 3.3. Thermal analysis

The combustion synthesis and precursor calcination processes were investigated in a simultaneous thermogravimetricdifferential thermal analyzer (TG-DTA, BOIF WCT-1D) combined with a Fourier transform infrared spectrometer (FTIR, Bruker Tensor 27). The sample was heated in flowing air (120 mL min<sup>-1</sup>, STP) from the room temperature to 1000 °C with a high heating rate of 10 °C min<sup>-1</sup> to better simulate the dried precursor calcinations process in the muffle furnace, and held at 1000 °C for 30 min. The pyrolysis gases of solid precursors were instantly introduced from the TG-DTA to the FTIR by a heat tracing pipe at 150 °C to avoid the condensation of steam. Spectra were recorded with a temporal resolution of 10 s. The infrared absorption band was in the range of



Fig. 8. Typical FSEM (a) and TEM (b) micrographs (with a magnification of 200,000 in the original images) of nm-TiO<sub>2</sub> samples produced using flame synthesis.



Fig. 9. Schematic diagram of the fluidized-bed facility.

600–4000 cm<sup>-1</sup>. Because the gas concentration was proportional to the absorbance with a value < 0.7, the absorbance could be used to characterize the concentration of the gas products. These formed OC samples were also examined in terms of their CLOU behavior using the TG-DTA, with the temperature increased from the room temperature to 1000 °C at a heating rate of 5 °C min<sup>-1</sup> in N<sub>2</sub> atmosphere (120 mL min<sup>-1</sup>, STP).

#### 3.4. Cyclic oxygen release and uptake tests

The capacity for repeated release and uptake of gaseous O<sub>2</sub> was investigated by successive oxygen release/uptake cycle tests in the TG-DTA. A small amount (~30 mg) of each OC sample was placed in a zirconia sample holder and brought from the room temperature to 900 °C at a heating rate of 5 °C min<sup>-1</sup> under air flow. After stabilization, 15 cycle tests were conducted continuously under conditions of alternating atmospheres, and temperature was held at 900 °C. The oxygen release and uptake atmosphere was pure N<sub>2</sub> and 21 vol% O<sub>2</sub> (balanced with N<sub>2</sub>), respectively, both with a flow rate of 120 mL min<sup>-1</sup> (STP) for 20 min.

#### 3.5. Cyclic reduction and oxidation tests

Temperature-programmed reduction (TPR) and temperature-programmed oxidation (TPO) studies were performed in a chemisorption analyzer (Micromeritics AutoChem II 2920). Each sample was heated in a 10 vol% H<sub>2</sub>/Ar flow (TPR) or 3 vol% O<sub>2</sub>/He flow (TPO) with 50 mL min<sup>-1</sup> (STP) from the room temperature to 900 °C at 10 °C min<sup>-1</sup>, and the final temperature was kept at 900 °C for 30 min. The off-gas was first led to a cold trap to remove the steam and then was introduced to the thermal conductivity detector (TCD). A TPR-TPO-TPR three-stage test with 150 mg of sample was conducted. TPR/TPO analysis was used to provide information on the reducibility species of the OC.

The cyclic redox tests of many more OC particles were carried out in a batch fluidized bed reactor (FBR) with methane as gaseous fuel to investigate the reactivity of OCs in a fluidization environment and the behavior with respect to agglomeration and attrition phenomena. An overview of the fluidized bed system was presented in Fig. 9. The detailed description of this system can be found in our published papers [41,42]. The FBR was fed with a batch of 20 g OC particles, and then the bed was heated to 850 °C, fluidized by air to ensure full oxidation of OC particles before cyclic redox tests. The OC particles were then exposed to 10 successive redox cycles with each cycle consisting of four stages: (1) purging with inert N<sub>2</sub> (800 mL min<sup>-1</sup>, STP) at 950 °C for 3 min; (2) reduction of the OC in CH<sub>4</sub> (500 mL min<sup>-1</sup>, STP) at 950 °C for 40 s; (3) purging with inert N<sub>2</sub> (800 mL min<sup>-1</sup>, STP) at 950 °C for 15 min; (4) oxidation of OC with air (800 mL min<sup>-1</sup>, STP) at 850 °C for 20 min.

#### 4. Results and discussion

# 4.1. Oxygen uncoupling of the OCs

Four samples (A, B, C and D) were examined in terms of their CLOU behavior using the TG-DTA under the same experimental conditions. The weight loss curves as a function of time, which can reflect the oxygen uncoupling capacity and reactivity of OCs, were shown in Fig. 10. All the TG data were normalized from the stable point at approximately 700 °C, after which the weight became stable and gaseous O2 release started. Clearly the OC (sample A) without adding nm-TiO<sub>2</sub> demonstrated the minimum final weight loss ( $\sim$ 6 wt%), whereas other oxygen carriers (samples B, C, D) with the addition of nm-TiO<sub>2</sub> demonstrated a larger oxygen transport capability, very close to the theoretical maximum value of loss weight (7.75 wt%). The sample D, CuO/TiO<sub>2</sub>, exhibited the highest maximum reduction rate, followed by samples B, C and A, and the experimental results were consistent with earlier DFT predictions. CuAl<sub>2</sub>O<sub>4</sub> appeared to be formed as a major phase except CuO for sample A with the 60 wt% CuO-40 wt% CuAl<sub>2</sub>O<sub>4</sub> mixture, according to the stoichiometric and XRD patterns (see Section 4.4, Fig. 16). In the reduction stage, CuO was reduced to  $Cu_2O$  and a small part of  $CuAl_2O_4$  also decomposed into  $CuAlO_2$ ,  $Al_2O_3$  and  $O_2$  according to the following reaction:

$$4CuAl_2O_4 \rightarrow 4CuAlO_2 + 2Al_2O_3 + O_2 \tag{R1}$$

For a fixed temperature, the equilibrium  $O_2$  partial pressure and the rate of gaseous  $O_2$  release of CuAl<sub>2</sub> $O_4$  is much lower than those of pure CuO [15]. Consequently, sample A gave a much slower rate of oxygen release, and the decomposition was not complete over the isothermal stage at 1000 °C for 30 min. In practical CL processes, fast cyclic reduction and oxidation of the oxygen carrier will be performed by circulating between two reactors, so the slow kinetics of  $O_2$  release from CuAl<sub>2</sub> $O_4$  are not favorable and essentially do not contribute to the gaseous  $O_2$  release. In contrast, samples B, C, and D showed fast stages of weight loss up to approximately 7.75%, proving that the nm-TiO<sub>2</sub> additive is effective in preventing



 $\ensuremath{\textit{Fig. 10}}$  TG and differential thermogravimetry (DTG) curves of four types of Cubased OCs.

the formation of  $CuAl_2O_4$  spinel and improving the reactivity of Cu-based OCs.

Furthermore, to investigate the cyclic CLOU performance, 15 consecutive release-uptake cycle tests for four types of OCs were conducted in the TG-DTA at 900 °C (the TG curves shown in Fig. 11). Obviously, samples A (CuO/Al<sub>2</sub>O<sub>3</sub>) and D (CuO/TiO<sub>2</sub>) showed unstable patterns in the extent of reduction and oxidation reactions, whereas the Cu-based OC supported by the TiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> composite demonstrated a good recyclability to release and absorb gaseous oxygen repeatedly. More specifically, reactivity evaluation was obtained through analyzing the TG data of the OC samples. The conversions of the OC reduction and oxidation as functions of time were calculated, respectively by:

$$X_{\rm red}(t) = \frac{m_{\rm ox} - m(t)}{m_{\rm ox} - m_{\rm red}} \tag{6}$$

$$X_{\rm ox}(t) = \frac{m(t) - m_{\rm red}}{m_{\rm ox} - m_{\rm red}}$$
(7)

where  $m_{\text{ox}}$ ,  $m_{\text{red}}$ , and m(t) are the OC weights at the fully oxidized state, the reduced form, and the actual weight at time t, respectively. The theoretical oxygen transport capacity for the OC was defined as

$$R_0 = \frac{m_{\rm ox} - m_{\rm red}}{m_{\rm ox}} \tag{8}$$

The actual oxygen (AO) transport capacity was defined as

$$R_{\rm AO} = R_{\rm O} X_{\rm max} \tag{9}$$

where  $X_{\text{max}}$  is the maximum conversion in cyclic TG tests. The oxygen transport rate was

$$r_0 = R_0 \cdot \frac{\mathrm{d}X}{\mathrm{d}t} \tag{10}$$

Figure 12 showed the actual oxygen transport capacities and rates in 15-cycle redox tests of the four samples. The oxygen transport rates were calculated as average values from 20% to 80% of the



Fig. 11. Weight changes of four types of Cu-based OCs during the cyclic reduction-oxidation TG tests.

conversion. There was a decrease in oxygen capacity for sample A with an increasing number of cycles. The mass of the oxidized and reduced state declined gradually with the cycle numbers. Factually,  $CuAl_2O_4$  spinel was formed in the fresh sample A due to the solid-solid reaction of CuO and  $Al_2O_3$  upon synthesis in air, and the product  $CuAlO_2$  of  $CuAl_2O_4$  decomposition (R1) even did not oxidize fully in the later  $O_2$  uptake.

With respect to sample B, support on  $\mu$ m-Al<sub>2</sub>O<sub>3</sub> (17.5 wt%) and nm-TiO<sub>2</sub> (5.0 wt%) showed the best stability. The amount of active component CuO always remained high-loading in the redox cycles, without observation of obvious XRD peaks of CuAl<sub>2</sub>O<sub>4</sub> (see Section 4.4, Fig. 16) because the nm-TiO<sub>2</sub> shell prevented the interaction between copper and aluminum phases. The actual oxygen transport capacity of sample B maintained approximately 0.075 kg O<sub>2</sub>/kg OC and was close to the theoretical value  $0.0775 \text{ kg O}_2/\text{kg OC}$ , corresponding well to the stable rates. The rate of O<sub>2</sub> release is dominated mainly by the crystalline CuO, and a higher content of crystalline CuO gives higher gaseous O<sub>2</sub> releasing capacity. A moderate declining tendency in oxygen release/uptake capacity was observed for sample C, and an ascending tendency in oxygen release/uptake capacity was observed for sample D. It was noted that sample D showed a very different tendency compared to others, and the oxygen release rate of each single cycle showed an increase with cycling progresses likely because of the development of fissures led to a rise in porosity and reaction surface. The reactivity increased up to a maximum value after several cycles and stabilized. It had previously been observed in ilmenite as an OC in CLC [43]. A similar effect was also observed in the field of carbonate looping for CO<sub>2</sub> capture where it was named "self-activation" [44]. When nm-TiO<sub>2</sub> was used for most or all of the support, the total oxygen release/uptake capacity was slightly less than expected. A possible reason for the discrepancy is that a high proportion of the TiO<sub>2</sub> additive is unfavorable for inhibiting sintering because the adsorption energy of TiO<sub>2</sub> is lower than the adsorption energy of the Al<sub>2</sub>O<sub>3</sub> as in the above-mentioned DFT calculations. In addition, too many or too few nm-TiO<sub>2</sub> can be harmful to the formation of complete core-shell structures. For an excessive TiO<sub>2</sub> additive, nm-TiO<sub>2</sub> will form larger agglomerates in aqueous suspension, also not conducive to inhibiting sintering according to the Zener pinning theory. In this context, the experimental results should not be surprising because sintering would lead to a decline in the active oxygen capacity and oxygen release/uptake rate.

# 4.2. Reactivity and stability of the OCs

Based on TGA tests and physicochemical characterizations (see Section 4.3), sample B was the optimal one and most worth to be further investigated, and hereafter sample A or sample E was used as a baseline for comparative studies. For the TPR-TPO-TPR experiments of sample B at the chemisorption analyzer, the TCD curves of two TPR experiments (shown in Fig. 13) demonstrated similar



Fig. 12. Reversible oxygen transport capacities and rates of four OCs in TG cyclic redox tests: (a) Oxygen release capacity; (b) Oxygen uptake capacity; (c) Oxygen release rate; and (d) Oxygen uptake rate.



Fig. 13. TCD profiles of TPR (10% H<sub>2</sub> + Ar) and TPO (3% O<sub>2</sub> + He) tests for sample A and sample B in the chemisorption analyzer.

shapes with same peak numbers and approximate peak temperatures (approximately 300 °C, attributed to the reduction reaction between CuO and H<sub>2</sub>), meaning nearly the same amount of H<sub>2</sub> consumption and then good chemical stability for sample B. For sample A (used as a baseline for comparison with sample B), the TCD profiles of two TPR experiments exhibited a main peak approximately 300 °C and a significantly smaller peak at higher temperatures (900 °C for the 1st TPR and 600 °C for the 2nd) due to the reduction reaction between CuAl<sub>2</sub>O<sub>4</sub> and H<sub>2</sub>. The two TPR tests also showed sample A is not stable in reactivity. From the TCD profiles of TPO experiments of the two samples, sample B absorbs more gaseous oxygen in the oxidation process.

We tested the CLC behavior of sample B with methane and resistance to agglomeration/sintering in a high-temperature (850–950 °C) environment using a batch fluidized bed reactor. Sample E (sol–gel) was used as a comparison based on our previous systemic research for sol–gel synthesis OCs. Ten successive redox cycles were conducted using 20 g OCs where the particles were subjected to a flow of 500 mL min<sup>-1</sup> pure CH<sub>4</sub> for 40 s during the reduction period. The reactivity of a given OC during reduction with methane quantified in terms of OC conversion rate as a function of time was calculated from the outlet gas concentrations by [45]:

$$\frac{dX}{dt} = \frac{1}{M_0 P_{\text{tot}}} n_{\text{in,CH}_4} (4p_{\text{CO}_2,\text{out}} + 3p_{\text{CO},\text{out}} - p_{\text{H}_2,\text{out}})$$
(11)

where  $M_0$  is the number of moles of active oxygen in the unreacted oxygen carrier;  $P_{tot}$  is the total pressure;  $n_{in,CH_4}$  is the molar flow of dry CH<sub>4</sub> entering the reactor;  $p_{CO_2,out}$ ,  $p_{CO,out}$ , and  $p_{H_2,out}$  are the outlet partial pressures of CO<sub>2</sub>, CO, and H<sub>2</sub>, respectively, after removal of water vapor. To be able to compare oxygen carriers with different fractions of support materials, a mass-based conversion,  $\omega$ , was defined as follows [45]:

$$\omega = \frac{m}{m_{\rm ox}} = 1 + R_0 (X - 1) \tag{12}$$

where  $R_0$  is the oxygen ratio

$$R_0 = \frac{m_{\rm ox} - m_{\rm red}}{m_{\rm ox}} \tag{13}$$

Figure 14 showed the OC conversion rate as a function of the mass-based conversion of sample B and sample E for the 2nd and 10th repeated cycles. Sample B demonstrated a higher conversion rate, close to complete conversion of the fuel because Sample B had a higher porosity of particles and almost all of the copper exists in



**Fig. 14.** Reactivity of OCs with methane as the fuel at 950 °C. Gas conversion rate as a function of the mass-based conversion for Sample B and Sample E.

the form of an active component, which has been confirmed by surface area, pore volume and XRD characterization (see Section 4.4).

In addition to reactivity, other aspects like agglomeration and attrition should be considered to evaluate the behavior of the OCs during tests at high-temperature fluidization. Figure 15 showed the particle size distribution (PSD) of both fresh and extracted particles from the reactors at the end of the cyclic tests. Sample B particles exhibited inconspicuous fragmentation and agglomeration, whereas sample E particles performed a little obvious agglomeration and attrition in spite of the high operating temperature, and defluidization of the reactors was never detected for two OCs.

In the continuous fluidization operation for CLC/CLOU, Cu-based OCs are always subjected to attrition trouble [46]. It has long been known that for fluidized bed combustion, particles from the fuel (coal, char, ash, *etc.*) or the SO<sub>2</sub> sorbent (limestone, dolomite, *etc.*) are also attrited by the mechanical forces in the bed, while chemical reactions are taking place [47]. To some extent, the mechanical damage and chemical corrosion of OC particles can be alleviated by designing proper inner structure as well as choosing suitable material component. In light of this, a hierarchical structure is consisted with a whole porous Al<sub>2</sub>O<sub>3</sub> core, an interconnected TiO<sub>2</sub> nanoparticle layer, and a Cu-based active component coat, which exhibits better mechanical strength and support inertness in comparison to conventionally synthesized samples of the same composition.

In order to validate the effect of SATCS, sample B as the optimal one was compared with other Al<sub>2</sub>O<sub>3</sub>- or TiO<sub>2</sub>-supported Cu-based OCs prepared by different methods available in some published literatures. Remarkably, sample B could be decomposed at an oxygen release rate up to 0.37 kg O<sub>2</sub>/(kg OC min) at 900 °C, about 11 and 18 times higher than these of CuO/Al<sub>2</sub>O<sub>3</sub> sample (80 wt% CuO loading at a 0.032 kg O<sub>2</sub>/(kg OC min) rate at 950 °C) [48] and CuO/TiO<sub>2</sub> sample (50 wt% CuO loading at a 0.02 kg O<sub>2</sub>/(kg OC min) rate at 900 °C) [49], respectively. For CLC in a fluidized-bed reactor, an estimate of the mass of OC needed in reactor,  $m_{bed}$ , can be calculated as [50]:

$$m_{\rm bed} = \frac{\omega \dot{m}_0}{d\omega/dt} \tag{14}$$

where  $\dot{m}_0$  is the stoichiometric mass flow of oxygen needed for complete conversion of the methane to carbon dioxide and water. Thereby, the amount of OC necessary can be calculated, in which 41.9 kg/MW<sub>th</sub> of sample B was much lower than 78 kg/MW<sub>th</sub> of a representative CuO/Al<sub>2</sub>O<sub>3</sub> sample in reference [9]. Moreover, the oxygen carrier recirculation rate between the air and fuel reactors is [50]

$$\dot{m}_{\rm sol} = \frac{\omega_{\rm air} \dot{m}_{\rm 0}}{\Delta \omega} \tag{15}$$



**Fig. 15.** Particle size distributions of fresh particles and particles after 10-cycles, OC extracted from the bed at the end of the tests: (a) sample B; (b) sample E (sol-gel).

where  $\omega_{air}$  is the conversion in the air reactor. Thus, for a  $\Delta \omega$  of 0.03 the needed recirculation rates of sample B and the CuO/Al<sub>2</sub>O<sub>3</sub> sample [9] would be 1.1 kg/(MW<sub>th</sub> s) and 2.6 kg/(MW<sub>th</sub> s), respectively. These results indicated that the reactivity of sample B was superior to that of these OCs prepared by conventional methods. Because there were many notable differences between these references and this work in experimental conditions (especially conditions such as temperature, atmosphere, and particle size, which all have a significant impact on reactivity), a comprehensive comparative investigation for some well-known preparation methods at the same experimental condition could be schematized in the near future. However, one point was affirmative that the conventional methods, such as mechanical mixing or freeze-granulation, fail to construct an effective microstructure maintaining higher dispersion level and facilitating active oxygen transmission. The analysis of physicochemical characterizations could confirm the inner organization form of the novel OC as well as provide a clear understanding for the SATCS method.

# 4.3. Physicochemical characterizations of the OCs

As shown in Fig. 16, the chemical compositions of Sample A and Sample B in three different states were analyzed using XRD. For sample A without nm-TiO<sub>2</sub>, CuAl<sub>2</sub>O<sub>4</sub> spinel was formed at high temperatures during synthesis as the reaction:

$$CuO + Al_2O_3 \rightarrow CuAl_2O_4 \tag{R2}$$



Fig. 16. XRD patterns of Sample A (left, CuO(77.5 wt%)/Al<sub>2</sub>O<sub>3</sub>(22.5 wt%)) and Sample B (right, CuO(77.5 wt%)/TiO<sub>2</sub>(5 wt%)-Al<sub>2</sub>O<sub>3</sub>(17.5 wt%)).



**Fig. 17.** Crushing strength of fresh and used Cu-based OCs. The vertical bars represent standard deviation of 30 repeated measurements for each sample.

The phase field in the Cu-Al-O system is dependent on the oxygen partial pressure during redox cycles in the temperature range of relevance [16].  $CuAl_2O_4$  could slowly release gaseous  $O_2$  as a possible reaction (R1), so only a few  $CuAl_2O_4$  would release oxygen for a limited time in CLOU process. As for Sample B, all of the copper was presented in the form of active phase  $CuO/Cu_2O$  to quickly achieve

#### Table 3

Properties of the OC particles, fresh and after 15 redox cycles.

complete redox, whereas TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> as support phases always maintained a stable chemical property.

As shown in Fig. 17, the crushing strength of four used samples was reduced, and the standard deviation of the measurement also decreased. However, Sample B had the highest strength and kept a higher mechanical stability that was good for attrition resistance and sintering resistance. A recent investigation has shown that OCs with a crushing strength above 1 N have generally shown better performance with respect to attrition in continuous operation, and with a crushing strength above 2 N are more likely to resist attrition than soft particles [45].

The attrition rate (by the standard abrasion tester), specific surface area (SSA) and specific pore volume (SPV) were measured and shown in Table 3. Attrition rate is a useful measure to estimate the lifetime of OC particles [14]. The attrition test was consistent with the crushing strength test, indicating that Sample B particles are really higher in mechanical durability. A higher specific surface area and specific pore volume of Sample B is an immediate cause of good reactivity. The fact that Sample B maintained high surface area and pore volume after 15 redox cycles further proved that Sample B had excellent resistance to sintering.

From above experimental results, we found that the addition of nm-TiO<sub>2</sub> has greatly improved the physicochemical performances of the Cu-based OC, and Sample B is the best from the point of view of CLOU behavior and material cost. Sample B was then selected for

	Sample A		Sample B		Sample C		Sample D	
	Fresh	15 Redox						
Attrition rate (%/h)	8.04	-	6.12	-	6.36	-	13.44	-
SSA (m <sup>2</sup> /g)	0.93	0.41	1.64	1.25	1.12	0.76	1.07	0.55
SPV (cm <sup>3</sup> /g)	0.013	0.008	0.028	0.021	0.017	0.013	0.02	0.006





Fig. 18. FSEM-EDS images of fresh (a, c) and reused (b, d) OC particles (Sample B, CuO(77.5 wt%)@TiO<sub>2</sub>(5 wt%)-Al<sub>2</sub>O<sub>3</sub>(17.5 wt%)). BSE and EDS profiles of cross section particles (a, b), and SE images of the Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> skeleton (c, d).

further investigation and analysis. Figure 18a and b via FSEM-EDS showed that in Sample B the components and elements were distributed uniformly before and after the 15-redox test, and the active component CuO was enriched on the surface layer of particles. It should be noted that Cu(NO<sub>3</sub>)<sub>2</sub> solution could impregnate into µm-Al<sub>2</sub>O<sub>3</sub> particles with porous structure, and nm-TiO<sub>2</sub> could migrate through these micro pores due to drag forces induced by the receding liquid surface and capillary forces [51] during precursor drying. And nm-TiO<sub>2</sub> thereby adsorbed on the inner surface of µm-Al<sub>2</sub>O<sub>3</sub> to inhibit CuAl<sub>2</sub>O<sub>4</sub> generation. As results, FSEM-EDS images show that Cu and Ti elements are distributed over the whole particle. The high magnification images showed the fresh and reused OC particles both maintained a rich and guite uniform porous structure. Once the active component CuO has been dissolved by the ammonia-ammonium carbonate solution, the core-shell structured Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> supports formed a spongiform framework with rich interconnected mesopores (as shown in Fig. 18c and d via SE). The active component was filled in the mesopores and separated into fine grains, so the contact between grain and grain, grain and Al<sub>2</sub>O<sub>3</sub> was prevented. This special structure ensures that the oxygen carriers demonstrate higher reactivity, satisfactory mechanical properties and sintering resistance.

#### 4.4. Environmental and economic evaluation

Synthetic Cu-based OCs often used copper nitrate as the main raw material, and there is no doubt that the NO<sub>x</sub> emissions problem needs to be reconsidered.  $NO_x$  is a serious air pollutant, and its generation and emissions must be strictly limited. The TG-DTA-FTIR investigation for dried precursors of Sample B (as a representative of SATCS method) and Sample E (sol-gel method) was conducted to analyze and compare the precursor transformation and gas pollutant emissions in OC synthesis. For the Sample B precursor, the TG-DTA curves (Fig. 19a) indicated that the decomposition follows the loss of (1) hydrate water at approximately 100–200 °C (endothermic). (2) urea and nitrate combustion (exothermic, ignited at 212 °C). The fact that a very small amount of NO<sub>2</sub> was detected using FTIR at approximately 210 °C and then the concentration rapidly declined to near-zero levels, as shown in Fig. 20 (green dashed line), demonstrated that there was a little decomposition of copper nitrate and urea (reactions R3 and R4) before the ignition, and then the stable combustion no longer released NO<sub>2</sub> (reactions R5 and R6). Obviously, the SATCS method can significantly reduce or even eliminate<sup>1</sup> NO<sub>x</sub> emissions during OC synthesis processes, thereby providing an environment-friendly synthesis route. It is noted here ammonia (NH<sub>3</sub>) was widely used in selective non-catalytic reduction (SNCR) to reduce NO<sub>x</sub> to nitrogen and water (R5). The sharp exothermic peak (2) at 268.3 °C of the DTA curve was characterized as the typical combustion synthesis. For per kilogram of OC (Sample B) produced, combustion releases heat at approximately 1.5 kW h (estimated according to the standard molar enthalpy change  $\Delta H_m^{\Theta} = -1675.5 \text{ kJ mol}^{-1}$  for reaction R6). The instantaneous heat release and high flame temperature<sup>2</sup> (approximately 2000 °C [28,52]) benefited to exempt the calcination stage and heating equipment, shorten the production cycle and save energy consumption.

$$2Cu(NO_3)_2 \rightarrow 2CuO + 4NO_2 + O_2 \tag{R3}$$



**Fig. 19.** TG-DTA curves for the temperature-programmed thermal decomposition of the dried precursors in air: (a) sample B, for DTA, (1) minimum (well) at 197.6 °C, (2) maximum (peak) at 268.3 °C; (b) Sample E (sol–gel), for DTA, three wells at (1) 124.6 °C, (2) 190.6 °C, (3) 268.8 °C, respectively, and one peak at (4) 967.5 °C.



**Fig. 20.** Relative concentration (measured using the FTIR and data processed using the OPUS 7.0 software) of NO<sub>2</sub> as a representative gaseous pollutant produced by the burning/calcining precursors.

$$CO(NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2 \tag{R4}$$

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$$
 (R5)

 $<sup>^1</sup>$  Note: for Sample B in the TG-DTA, as shown in Fig. 20, a little NO<sub>2</sub> release owing to incomplete reaction with NH<sub>3</sub> at low temperature before burning is observed. Actually, pre-ignition can prevent the NO<sub>2</sub> release.

<sup>&</sup>lt;sup>2</sup> Note: for Sample B, in the TG-DTA, the temperature was measured out of the sample holder with a small amount ( $\sim$ 60 mg) of sample and high heat dissipation, thus it was much lower than the actual combustion temperature.

Table 4	
Raw material costs of	of fresh OCs.

	Unit price (\$/kg)	Sample B (SATCS)		Sample E (sol-gel)		
		Amount (kg/kg O <sub>2</sub> )	Cost (\$/kg O <sub>2</sub> )	Amount (kg/kg O <sub>2</sub> )	Cost (\$/kg O <sub>2</sub> )	
μm-Al <sub>2</sub> O <sub>3</sub>	0.5 <sup>a</sup>	2.30	1.2	_	-	
nm-TiO <sub>2</sub>	20 <sup>b</sup>	0.66	13.2	-	-	
$CO(NH_2)_2$	0.2 <sup>c</sup>	12.83	2.6	-	-	
$Cu(NO_3)_2 \cdot 3H_2O$	4.6 <sup>d</sup>	30.98	142.5	38.99	179.4	
$Al(C_3H_7O)_3$	3.7 <sup>e</sup>	-	-	26.53	98.2	
OC product	-	13.16	159.5	16.56	277.6	

<sup>a</sup> http://jzcshg.en.made-in-china.com/product/WSlQXaHwLIVO/China-High-Purity-White-Aluminum-Oxide.html.

<sup>b</sup> http://ahelite.en.made-in-china.com/product/jqsnvKdDwBpu/China-10nm-Nano-Titanium-Dioxide-for-Photocatalyst-NT10.html.

<sup>c</sup> http://qingshang.en.made-in-china.com/product/lvUnFfA|vkcz/China-Nitrogen-Fertilizer-Urea-46.html.

<sup>d</sup> http://xilongchemical.en.made-in-china.com/product/yKDxvTcUHrVz/China-99-Purity-Cupric-Nitrate-Ar-Grade.html.

<sup>e</sup> http://www.made-in-china.com/showroom/jintachem/product-detailHMUEZOguMNkw/China-Aluminium-Isopropoxide.html.

 $3Cu(NO_3)_2 + 5CO(NH_2)_2 \rightarrow 3CuO + 5CO_2 + 10H_2O + 8N_2$  (R6)

For Sample E in Fig. 19b, the removal of capillary water (well (1)) and hydrate water (well (2)), and the decomposition of copper nitrate (well (3)) need large amounts of heat consumption, and even worse, generate large amounts of released NO<sub>2</sub> as much as 18.3 mol/kg OC (Fig. 20 pink solid line) and would cause serious air pollution if no effective treatment. In addition, a weak exothermic peak (Fig. 19b peak (4)) started from approximately 800 °C until the end of the calcination, owing to the formation of copper aluminate (reaction R2). This is a drawback in conventional synthesis methods for Cu-based OCs, whereas the phenomenon does not happen in SATCS.

Furthermore, the impact of the nm-TiO<sub>2</sub> additive on the manufacturing cost of fresh OC is worth considering. In Table 4, the unit prices of raw materials sourced from the industry information products about manufacturers, suppliers and website (www.made-in-china.com) in August 2014, and the costs of OCs for per kilogram gaseous oxygen capacity were estimated. The price adopted here approaches to the median over the past 7 years and is a representative choice at least. Obviously, the cost of Sample B was far lower than the cost of Sample E, and a cost advantage for the SATCS method compared with the sol-gel method was indicated. The cost of nm-TiO<sub>2</sub> was only approximately 8% of the total raw materials cost, which did not affect total costs so dramatically. If the environmental cost and energy consumption were considered, the superiority of the SATCS method was particularly prominent, and the costs could be cut further in mass production.

# 5. Conclusions

This study aimed to prepare Cu-based OCs with a high loading and high degree of dispersion of active CuO in the inexpensive and durable support. A novel Cu-based oxygen carrier (CuO@TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) with high performance was reported based on an interesting synthetic route (SATCS), involving nanomaterial, colloid chemistry and environmental protection. The tailor-made CuO@TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> OC particles demonstrated satisfactory performances as desired in the CL processes. It is possible to synthesize functional OCs for the CL processes by tuning the precursor chemistry and fabricating the microstructures within particles.

First, a basic understanding of the interaction between CuO and support was obtained via DFT calculations, which involved the reactivity and sintering resistance of Cu-based OCs and was helpful in selecting the proper materials (i.e.,  $TiO_2$  and  $Al_2O_3$ ). Then, the influence of support size and content on OC stability was analyzed based on the concept of the Zener pinning force of sintering limit, which suggested that adding nanolevel particles favored sintering resistance. Subsequently, colloid chemistry analysis and calculations were used for designing an expected orderly microstructure, in which active component CuO was supported by core–shell structured  $Al_2O_3$ –TiO<sub>2</sub> composite (a core( $Al_2O_3$ )–shell(TiO<sub>2</sub>) hierarchical structure customized from the self-assembly of flame-synthesized TiO<sub>2</sub> nanoparticles and commercial  $Al_2O_3$  microparticles). Finally, OCs were efficiently manufactured with a short production period, low energy consumption and low pollution using the combustion synthesis technique.

The novel CuO@TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> OCs with different Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> contents were examined in both a thermogravimetric analyzer and a fluidized bed reactor to investigate the oxygen transport capacity, reactivity, and cyclic oxygen release and uptake. A representative Cu-based OC based on a support composite of Al<sub>2</sub>O<sub>3</sub> (17.5 wt%)-TiO<sub>2</sub> (5 wt%) exhibited excellent performance of repeated oxygen release/uptake, stable mechanical strength, and high reactivity. The microstructure and phase analysis using FSEM-EDS and XRD showed that the Al<sub>2</sub>O<sub>3</sub> surface was coated with TiO<sub>2</sub> nanoparticles, resulting in a spongy but firm inert framework. The CuO was uniformly dispersed and highly loaded in the sponge framework. The addition of TiO<sub>2</sub> nanoparticles can prevent the interaction between CuO and Al<sub>2</sub>O<sub>3</sub> almost completely and can inhibit CuO grain sintering effectively, so OCs with a high CuO content can withstand a higher temperature (such as 1000 °C) without sintering and agglomeration.

Thus, CuO@TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> is an attractive oxygen carrier for CL processes, and the SATCS method is highly suitable for large-scale preparation of OC particles. The high performance OC could be applied in CLC, CLOU, CLAS, and Ca–Cu looping for clean energy production and CO<sub>2</sub> capture.

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