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# Characterization and evaluation of Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> oxygen carrier prepared by sol-gel combustion synthesis

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#### ABSTRACT

The sol-gel combustion synthesis (SGCS) for oxygen carrier (OC) to be used in chemical looping combustion (CLC) was first designed and experimented in this work, which is a new method of OC synthesis by combining sol-gel technique and solution combustion synthesis. Cheap hydrated metal nitrates and urea were adopted as precursors to prepare Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> OC at the molar ratio to unity (Fe1Al1), which was characterized through various means, including Fourier transforms infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), differential thermal analysis (DTA), X-ray diffractor (XRD), and N<sub>2</sub> isothermal adsorption/desorption method. FTIR analysis on the chemical structure of the dried gel of Fe1Al1 indicated that urea was partly hydrolyzed and the hydrated basic carbonate was formed by the combination of groups such as  $(Fe(_{1-y}AI_y)_{1-x}O_{1-3x}, CO_3^{2-})$  and -OH-. By analyzing the staged products during SGCS, calcination was found as a necessary step to produce Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> OC with separate phases of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Through TGA–DTA, the decomposition of the dried gel was found to undergo five stages. The analysis of the evolved gases from the gel decomposition using FTIR partially confirmed the staged decomposition and assisted a better understanding of the mechanism of SGCS. XRD identification further substantiated the necessity of calcination to synthesize Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> OC with separate phases of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, though it was not necessary for the synthesis of single phase  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Structural characterization performed on  $N_2$  adsorption analyzer displayed that the pore shape of Fe1Al1 particles was heterogeneous. Finally, H<sub>2</sub> temperature-programmed reduction (TPR) of Fe1Al1 products in TGA indicated that the reduction reaction of Fe1Al1 OC after calcination was a single step reaction from  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> to Fe, and calcination benefited to improve the transfer rate of the lattice oxygen from the OC to fuel H<sub>2</sub>. Furthermore, four times of reduction and oxidization (redox) reaction by alternating with H<sub>2</sub> and air demonstrated the synthesized OC had good reactivity and sintering-resistance, much suitable to be used in the realistic CLC. Overall, the SGCS method was found superior to other existent methods to prepare Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> OC for CLC application.

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#### 1. Introduction

Chemical looping combustion (CLC) technology has received great recognition for its distinguishable advantages in abating CO<sub>2</sub> emission from carbonaceous fuel combustion, through inherent CO<sub>2</sub> separation. The CLC system is basically composed of two reactors, an air reactor (AR) and a fuel reactor (FR). In the FR, the oxygen carriers, such as metal oxides  $M_xO_y$  instead of the air in the normal combustion, are reduced with the fuel. In the AR, the reduced metal oxides  $M_xO_{y-1}$  are oxidized with the introduced air, and then the

\* Corresponding author at: Institute of Environmental Science and Engineering, Nanyang Technological University, Innovation Center, Block 2, Unit 237, 18 Nanyang Drive, Singapore 637723, Singapore. Tel.: +65 67943244; fax: +65 67921291. fully oxidized metal oxides  $M_xO_y$  in the AR are transported back to FR, as shown in Fig. 1. This reduction and oxidation process (redox process) can be repeated for many times. During the multicycles of transportation between FR and AR, oxygen carriers have to suffer the thermal shock and mechanical abrasion, and thus cause serious sintering and fragmentation, which lead to great loss in the reactivity of the oxygen carriers. Obviously, in CLC studies, advances of oxygen carriers with good reactivity and strong performance to combat sintering, are crucial to the real application of this novel  $CO_2$  control technology [1,2]. The performance of oxygen carriers is closely associated with the related preparation methods. Great drawbacks in the current various preparation methods of OC entail the necessity to develop novel preparation methods.

Different types of oxygen carrier have been investigated. The mostly studied ones are generally composed of active metal oxides and inert supports, where metal oxides provide the lattice oxy-

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Fig. 1. Scheme of chemical looping combustion (CLC), where  $M_x O_y / M_x O_{y-1}$  denotes the oxidized and reduced oxygen carriers, respectively.

gen to adequately oxidize the carbonaceous fuel into CO<sub>2</sub>, and the supports are needed to improve the resistance of oxygen carriers to fragmentation, abrasion and sintering. Till now, Ni, Cu, Fe, Mn, and Co-based oxides have been mainly adopted, and the former three oxides are more widely applied in CLC system. However, there are pros and cons associated with each metal and the oxide. NiO has high reactivity but thermodynamic limitation and concern of toxicity. CuO has exothermic characteristic but low melting point and possible defluidization as well as potential secondary pollution. Comparing to NiO and CuO, Fe<sub>2</sub>O<sub>3</sub> has a striking economical strength for its lower price, environmental benignity without potential pollution and higher melting points. Therefore, Fe<sub>2</sub>O<sub>3</sub> is adopted in this study as the active metal oxide for OC. On the other hand, a variety of materials, such as Al<sub>2</sub>O<sub>3</sub>, bentonite, MgO, SiO<sub>2</sub>, ZrO<sub>2</sub>, MgAl<sub>2</sub>O<sub>4</sub>, sepiolite and kaolin, have been reported as inert supports for different oxygen carriers. Considering the reactivity, fragmentation and avoidance of the interaction between Fe<sub>2</sub>O<sub>3</sub> and inert supports, Al<sub>2</sub>O<sub>3</sub> is recognized as one of the most promising supports [1,2]. Furthermore, for the synthesis of Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> OC with good performance, the optimized molar ratio of Fe<sub>2</sub>O<sub>3</sub> to Al<sub>2</sub>O<sub>3</sub> was around unity [3,4] to compensate between the good resistance to sintering and fragmentation from the inert support Al<sub>2</sub>O<sub>3</sub> and sufficient lattice oxygen capacity from the active metal oxide Fe<sub>2</sub>O<sub>3</sub> [3,4].

Currently, there are two main options available for preparing oxygen carriers: "dry chemistry" and "wet chemistry" routes [5–7]. Taken the synthesis of  $Fe_2O_3/Al_2O_3$  OC as an example, the former preparation option includes mechanical mixing [1], freezegranulation [8] and impregnation [9]. On the other hand, the "wet chemistry" options for the preparation of oxygen carriers are more advantageous for the uniformly mixing between metal oxides and supports at the molecular scale, the lower cost of the precursors and the accuracy of the desired stoichiometric amount to be reached. The "wet" preparation methods involved for the synthesis of oxygen carriers are co-precipitation [10], micro-emulsion [11], sol-gel method [12,13], dissolution [14,15], and solution combustion synthesis method [16,17]. Among these methods, sol-gel is one of the most promising routes because the oxygen carriers synthesized by the method are fine and uniform, with strong mechanical strength and high attrition resistance, but expensive alkoxides have to be adopted [12,13]. To avoid using expensive alkoxides, dissolution method was designed by Ishida et al. [14] and later followed by Readman et al. [15] using 2-propanol and metal nitrate to substitute metal alkoxides.

Different from all the aforementioned preparation methods, solution combustion synthesis is relying on a self-sustained combustion reaction between metal nitrates as the oxidizer and various organic fuels (e.g., citric acid and glycine) to produce nano-scaled metal oxide powders [16–18]. Due to the solution mixture of the precursors used and the exothermicity of the combustion reaction, this method displays prominent advantages than other "wet chemistry" methods for its rapidity and simplicity of the synthesizing process, lower energy requirement and molecular mixing of the precursors [19]. Therefore, it would be advantageous and promising

to combine the sol-gel method and solution combustion synthesis method to produce OC with an expected good performance for CLC application.

Previous studies on preparation of  $Fe_2O_3$  [20–22] or  $Al_2O_3$ [23–25] alone have been reported through different methods including solution combustion synthesis using different organic fuels. But information on the synthesis of  $Fe_2O_3/Al_2O_3$  composite particles are limited and the methods of preparing  $Fe_2O_3/Al_2O_3$ particles are confined to impregnation [9], freeze-granulation [3], co-precipitation [26], and sol–gel method [27]. Researches on novel synthesis method for  $Fe_2O_3/Al_2O_3$  OC based on sol–gel and solution combustion synthesis method are greatly worthwhile.

In this research, a novel synthesis method of  $Fe_2O_3/Al_2O_3$  OC, designated as sol-gel combustion synthesis (SGCS) method, was firstly put forward and studied, using nitrates of iron and aluminum as the oxidizer and urea as the fuel. This preparation method was systematically researched, with focuses on the characterization of the as-synthesized  $Fe_2O_3/Al_2O_3$  OC, optimization of the SGCS process parameters, and evaluation of the performance for the synthesized  $Fe_2O_3/Al_2O_3$  OC, respectively. In this paper, the comprehensive characterization of the synthesized  $Fe_2O_3/Al_2O_3$  OC produced by SGCS at the molar ratio around unity (designated as Fe1Al1), was performed through various experimental means and the reduction activity of Fe1Al1 by H<sub>2</sub> was tested in TGA. The mechanism of SGCS was also preliminarily explored.

#### 2. Experimental procedures

#### 2.1. Selection of starting materials for SGCS

In comparison with the adoption of citric acid, glycine, etc. as fuel in solution combustion synthesis [15–17,19], urea was suggested as the most convenient fuel for its ready availability [6], high exothermicity [28] as well as effective complexation of amine group (i.e.,  $-NH_2$ ) from urea with transition metals [29]. In comparison to the corresponding sulfates or chlorides, metal nitrates were chosen as the suitable oxidizer for its good solubility in water and lower decomposition temperature. Hydrated nitrate was further preferred for its easy solubility [6] and less violence of the redox reaction between urea and nitrates. Therefore, the starting materials used in this research were Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (98%, Alfa Aesar), Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (98%, Sinopharm) and urea (98+%, Alfa Aesar).

#### 2.2. Synthesis of $Fe_2O_3/Al_2O_3$ oxygen carrier

Fe1Al1 OC was prepared by SGCS method through the following procedure. Firstly, stoichiometric compositions of metal nitrates (including  $Fe(NO_3)_3.9H_2O$  and  $Al(NO_3)_3.9H_2O$ ) and urea were calculated at the desired molar ratio on the basis of 0.03 mol of  $Fe(NO_3)_3.9H_2O$ . The molar ratio of  $Al(NO_3)_3.9H_2O$ , urea, and deionized (DI) water to  $Fe(NO_3)_3.9H_2O$  was correspondingly determined as 1, 5.2, and 46 by propellant chemistry theory to ensure that the equivalent ratio of the reducing valence of urea to the total oxidizing valence of nitrates was unity, and thus the heat released was at its maximum [30].

Calculated amounts of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and urea were accurately weighed and dissolved in DI water in a pyrex beaker. The mixture was then stirred on a hot plate (Cole Parmer model, 4803-00) exposed to air atmosphere inside a fume hood for good ventilation and aged at 75 °C until the formation of viscous colloidal suspension (sol) in yellowish red. During the formation of sol, the value of pH was periodically tested using the carefully calibrated pH meter (Mettler Toledo, Delta 320). Then, the viscous wet sol was dried at 80 °C and 135 °C sequentially in the temperatureprogrammed desiccator (Contherm Thermotec 2000) for different



Fig. 2. Flow chart for the synthesis of Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> OC by SGCS.

durations. Next, the so-prepared dried gel was transferred in a ceramic dish and ignited in the preheated muffle furnace (Kiln west, Falsaff Pty., Ltd.) in the fume hood at 600 °C for 15 min. Finally, the as-burned product proceeded to be calcined in the same furnace at 950 °C for 2 h. The flow chart for the procedure of SGCS to produce Fe1Al1 OC is presented in Fig. 2.

## 2.3. Characterization of the synthesized Fe $_2O_3/Al_2O_3$ oxygen carrier

The chemical structure of the products formed by SGCS during the different preparation stages was determined by infrared (IR) spectra on the Fourier transforms infrared Spectrometer (BioRad Excalibur Series, model FTS 3000) in the wave number range of  $4000-400 \text{ cm}^{-1}$ , with 64 scans at a spectral resolution of  $4 \text{ cm}^{-1}$ . Samples of IR analysis were prepared by mixing the samples with KBr at a mass ratio of 1:200 in a steel die.

The thermal decomposition behavior of the dried gel was simulated and examined via TGA–DTA in the instrument of Netzsch STA409C. The heating rate and the flow rate of air were set as 20 °C/min and 50 ml/min, respectively. The evolved gas species, dried through a portable tubular gas desiccator full of calcium sulfate dihydrate, were studied by FTIR coupled with TGA (TA 2050, USA) at the same experimental condition as that of TGA–DTA on STA 409C.

Phase identification of the as-burnt and the ensuing calcined products Fe1Al1 OC was performed through X-ray diffractor (XRD) BDX 3200 using Cu K $\alpha$  radiation at a scanning rate of 1°/min. The averaged crystalline size of the powders was evaluated employing the Scherrer formula [31] in Eq. (1).

$$D = \frac{0.9\lambda}{\beta \cos \theta} \tag{1}$$

where *D* is the crystallite size in nm,  $\lambda$  is the radiation wavelength (0.15406 nm for Cu K $\alpha$ ),  $\theta$  is the diffraction angle and  $\beta$  is the corrected half width for instrument broadening.

Structural characterization was carried out by analyzing the N<sub>2</sub> adsorption isotherms, obtained from the adsorption analyzer (Micrometrics ASAP 2020) at -196 °C. The specific surface area of the synthesized OC was calculated by the Brunauer–Emmett–Teller (BET) theory [32] using the linear part ( $0.0 < P/P_0 < 0.25$ ) of the adsorption branch on the assumption of a closely packed BET monolayer. The pore size distribution of the synthesized oxygen carriers was derived using Barrett–Joyner–Halenda (BJH) model [33] by calculation of the desorption branch of the isotherm. In addition to specific surface area and pore size distribution, surface fractal dimension (Ds) is also one of the specialties for various materials, because the surfaces of most materials are actually rough instead of absolutely smooth for their geometric irregularities and defects.



**Fig. 3.** Infrared spectrums of the formed Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> OC; (a) the dried gel; (b) the product after ignition; (c) the finished OC after calcination.

The roughness can be well characterized by fractal. And thus, in this research, the fractal dimension *Ds* for the synthesized OC using SGCS method was estimated using the simple adsorption method on the basis of the effect of capillary condensation [34], as shown in Eq. (2).

$$\ln\left(\frac{V}{V_m}\right) = K + (Ds - 3)\ln\left(\ln\left(\frac{P_0}{P}\right)\right)$$
(2)

where  $P_0$  and P are the saturation and equilibrium pressures, K is a characteristic constant,  $V_0$  and V are the gas volumes adsorped on the OC samples at the pressures  $P_0$  and P, respectively.

H<sub>2</sub>-temperature programmed reduction (TPR) with the synthesized Fe1Al1 OC were preliminarily studied on TGA (TA 2050, USA) using the mixture gas of  $H_2$  with  $N_2$  (50 vol%). The heating rate and the flow rate for the mixture gas were again set as 20°C/min and 50 ml/min, respectively. Furthermore, in order to evaluate the reactivity and sintering-resistant characteristics for the as-synthesized Fe1Al1 oxygen carrier using SGCS, four cyclic times of reducing and oxidizing reactions between as-sintered Fe1Al1 oxygen carrier in  $63-106 \,\mu\text{m}$  and alternating by H<sub>2</sub> in 50 vol% with balance N<sub>2</sub> and air were performed using thermogravimetric analyzer (TA 2050, US). In the prevention of the potential explosion between  $H_2$ and air by directly mixing, after the reducing reaction of Fe1Al1 oxygen carrier with H<sub>2</sub>, inert N<sub>2</sub> was introduced into the reaction chamber of the TGA 2050 for up to 2.5 min. The flow rates for H<sub>2</sub>, air and inert N<sub>2</sub> were fixed as 50 ml/min. And the reaction temperature was stabilized as 850 °C. Meanwhile, the microstructures of both the as-synthesized fresh and the reacted Fe1Al1 OC over four cyclic times of redox process were scanned at the Analytical & Testing Center with Huazhong University of Science & Technology using the field scanning electron microscopy(FSEM) image (Siron 200, Netherlands) with the accumulated voltage of 20 kV at the magnification of 5000.

#### 3. Results and discussion

#### 3.1. IR analysis of the synthesized products

Within the whole process for the synthesis of Fe1Al1 OC by SGCS, three typical preparation stages, including drying process in the desiccator, igniting and calcining in the muffle, were involved. The formed products after these three stages were designated as Fe1Al1gel, Fe1Al1ig, and Fe1Al1si, respectively. The FTIR spectra of these staged products are shown in the curves (a), (b) and (c) in Fig. 3.

Firstly, in the curve (a) for the dried gel of Fe1Al1 OC, the evolution of urea was analyzed. The strong broad peak around 3320 cm<sup>-1</sup>



Fig. 4. TG-DTA curves for the thermal decomposition of the dried gel for Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> OC under air atmosphere; (a) TG curve; (b) DTG-DTA curves.

and the sharp band at  $1758 \text{ cm}^{-1}$  were ascribed to  $\text{NH}_4^+$  group [35] and OCN<sup>-</sup> ion [36], respectively. The presence of both NH<sup>4+</sup> and OCN<sup>-</sup> ions clearly indicated the occurrence of the hydrolysis of urea during the preparation of Fe1Al1 OC using SGCS [36,37]. The bands at 825, 984, 1174 and 1384 cm<sup>-1</sup> were mainly ascribed to the bending vibration of ionic  $CO_3^{2-}$ , which resulted from the further hydrolyzed reaction of cyanate ion OCN<sup>-</sup> [36]. And the hydrolysis of OCN<sup>-</sup> was determined by the pH value of the aqueous solution, so in this research, the pH value of the aqueous solution was carefully inspected. It was observed that, at the initial preparation stage, the pH value was gradually increasing from around 1.5 to the constant value of 7.3 at the final stage with the formation of viscous sol. The variation trend of pH value observed was similar to the simulation of urea hydrolysis by Mavis and Akine [37]. In addition, the relatively weak bands at 532, 1040, 1157 and 1400  $\text{cm}^{-1}$  were ascribed correspondingly to the different vibration modes of groups CN and NH<sub>2</sub>, which implied the existence of free urea molecule in the dried gel without hydrolysis or decomposition.

On the other hand, the evolution of iron and aluminum nitrates in the SGCS was also analyzed. The band at  $678 \text{ cm}^{-1}$  was ascribed to the  $(\text{Fe}_{1-y}\text{Al}_y)_{1-x}\text{O}_{1-3x}$  group. It was the formation of this complex group that prevented the preferential precipitation of both ions of Fe<sup>3+</sup> and Al<sup>3+</sup> possibly involved in the co-precipitation [10]. And the complex was further formed through the hydrolysis of iron and aluminum ions and then was complexed with OH group and  $\text{CO}_3^{2-}$  [37,38], characterized as the hydrated basic carbonates [36]. Meanwhile, the band at 480 cm<sup>-1</sup> shows the formation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> [39].

Furthermore, according to the IR spectra in the curves (b) and (c) for the as-burnt and calcined Fe1Al1 OC, the significant decease or complete disappearance of the characteristic bands for  $CO_3^{2-}$ ,  $NH_4^+$ and  $NO_3^-$  ions suggested that those ions were removed during the ignition and calcination process. The newly generating bands at 653 cm<sup>-1</sup> for the as-burnt product and 626 cm<sup>-1</sup> for the calcined OC were ascribed to the iron aluminate and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> [40], respectively. The presence of iron aluminate after igniting process but disappearance in the calcined product indicated that calcining treatment was necessary to synthesize Fe1Al1 OC with separate phases of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> using SGCS. For simplicity, other bands and their assignments were listed in Table 1 as a reference.

#### 3.2. Thermal decomposition of the dried gel of Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> OC

In order to understand the potential transformation of the dried gel in the muffle furnace, TGA–DTA was performed at heating 20 °C/min from ambient temperature upward to 1300 °C under

air atmosphere. The evolved flue gas was studied using FTIR coupled with TGA 2050. The TGA–DTA results and the IR spectra are depicted in Figs. 4 and 5, respectively.

From Fig. 4a, the TG curve indicated that the mass of the dried gel decreased from 100% to 15.7% with the temperature increasing from the ambient to around 450 °C, suggesting the precursor decomposed completely below 450 °C to form various oxides. In Fig. 4b, although there only existed a noticeable DTG peak centering at 266.88 °C, four distinguishable peaks in the DTA curve occurred, centering at 145.94, 208.11, 258.48 and 312.64 °C, respectively. And the reactions related to the former three peaks were endothermic. Although either urea or ammonium nitrate alone was reported to easily decompose accompanying the mass loss around 200 °C[41], the presence of urea would postpone the decomposition of ammonium nitrate to higher temperatures up to 300 °C[41].

The fact that no ammonia (NH<sub>3</sub>), CO<sub>2</sub> or nitrous oxide was detected by FTIR at around 200 °C, further proved the decomposition of complex instead of free urea or ammonia nitrate, though the curve at 200 °C was not plotted in Fig. 5. As a result, the second endothermic peak around 200 °C in the DTA curve was reasonably supposed to be the dehydration of the intercalated water in the formed complex of dried gel. Then, the third endothermic peak around 258 °C, accompanied with the presence of CO<sub>2</sub> in Fig. 5, indicated the decomposition of  $CO_3^{2-}$  involved in the complex. Overall, based on the IR spectra of the evolved gases shown in Fig. 5, the former three peaks in DTA curves were mainly attributed to the two thermal dehydrations in sequence and the ensuing decomposition of  $CO_3^{2-}$  anion involved in the formed complex, similar to the decomposition of the hydrated basic nickel carbonate [36]. The fourth sharp exothermic reaction for the peak at 312.64 °C in the DTA curve was characterized as the typical combustion synthesis. The reaction involving urea and ammonium nitrate was listed



**Fig. 5.** Infrared spectra of gases products from the combustion of the gel of  $Fe_2O_3/Al_2O_3$  OC under air atmosphere.

#### Table 1

Infrared frequencies and band assignments of the dried gel, ignited and calcined products of Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> OC.

Species	Numbers	Frequency <sup>a</sup> (cm <sup>-1</sup> )	Assignments <sup>b</sup>	Refs.
Dried gel	1	3465-3174(s/sh)	$\nu(OH) + \nu(NH_4^+)/\nu(NH_2)$	[35,36]
	2	2370(m)	CO <sub>2</sub>	[55]
	3	2191(m)	ν (NCO)	[37]
	4	1758	ν(CO)	[56]
	5	1633(s)	δ(H–O–H)	[36]
	6	1400	$\nu(CN)$	[56]
	7	1383(s)	$\delta (CO_3^{2-}) + \nu (NO_3^{2-})$	[36,57]
	8	1158(m)	$\delta (CO_3^{2-}) + \rho (NH_2)$	[36,58]
	9	984(m)	$\delta$ (CO <sub>3</sub> <sup>2–</sup> )	[36]
	10	1004(m)	ν(CN)	[56]
	11	825(m)	$\delta (CO_3^{2-}) + \nu (NO_3^{2-})$	[36,57]
	12	678(w)	Fe-Al-O	[38]
	13	591	$\delta$ (NCO)	[56]
	14	532	$\delta$ (NCN)	[56]
	15	479(w)	Fe–O	[22]
Ignited product	2	2359(w)	CO <sub>2</sub>	[55]
	5	1384(m)	$\delta$ (CO <sub>3</sub> <sup>2–</sup> )	[36]
	9	653(s)	Fe–Al–O	[26]
	10	493(s)	Fe–O	[26]
Calcined product	2	2343(w)	CO <sub>2</sub>	[55]
	9	626(w)	Al-O	[26]
	10	444(m)	Fe–O	[26,40]
	11	572 (s)	Fe-O + Al-O	[26,40]

<sup>a</sup> s: strong; m: medium; w: weak; sh: shoulder.

<sup>b</sup>  $\nu$ ,  $\delta$  and  $\rho$  representing stretching vibration, bending vibration and in-plane bending vibration for the different chemical groups.

below:

$$CO(NH_2)_2 + NH_4NO_3 \rightarrow 2NH_3(g) + CO_2(g) + N_2O(g) + 4H_2O(g)(3)$$

According to Eq. (3), for SGCS with urea as the fuel, the oxidizer was actually provided by  $NH_4NO_3$  other than from metal nitrates as reported by Erri et al. in the synthesis of NiO-based OC using solution combustion synthesis [16,17,19]. In addition to the four peaks, there was also a broad endothermic peak around 900 °C in Fig. 4 without mass loss, which implied the phase transformation of the formed oxides [42].

The trend of gas evolving from the reaction of the dried gel under the air atmosphere was seen in Fig. 5. At 250 °C, the gases emitted were only H<sub>2</sub>O and CO<sub>2</sub>. With reaction temperature increasing to 300 °C, a little amount of NH<sub>3</sub> and N<sub>2</sub>O produced. But with the reaction temperature further increasing from 350 to 400 °C, both NH<sub>3</sub> and N<sub>2</sub>O cannot be detected, possibly due to the rigorous exothermic reaction between the emitted NH<sub>3</sub> and gaseous nitrous oxides NO<sub>x</sub>, as shown in Eq. (4) below [43].

$$4xNH_3(g) + 10NO_x(g) \rightarrow (5 + 2x)N_2(g) + 6xH_2O(g) + 2xO_2(g)(4)$$

The reaction between NH<sub>3</sub> and NO<sub>x</sub> could effectively avoid the potential pollution from the emitted detrimental gases during the synthesis of oxides. Meantime, the instantaneous heat release and high flame temperature (around 2000 °C) benefited to form the expected phases rapidly [23]. These two advantages from the adoption of the urea in SGCS, instead of other fuels in SGCS, are greatly beneficial for the synthesis of oxygen carrier, especially in mass production.

#### 3.3. Phase identification of the synthesized $Fe_2O_3/Al_2O_3$ OC

Phase identification of the as-burnt and finished Fe1Al1 OC after the ignition and calcination was performed using XRD, as shown in Fig. 6. The curves (a) and (b) were for Fe1Al1ig and Fe1Al1Si, respectively. In addition, as the reference cases, XRD patterns of the two separate phases prepared in lab, i.e.,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, were also provided and demonstrated in Fig. 6 in curves (c)–(f). These two separate phases were prepared following the same procedure as depicted in Fig. 1. From Fig. 6, after ignition, Fe1Al1ig consisted of Fe<sub>2</sub>O<sub>3</sub> and iron aluminate (Fe1Al1<sub>2</sub>O<sub>4</sub>) instead of Al<sub>2</sub>O<sub>3</sub>, due to aluminum substitution and the formation of the complex group (Fe<sub>1-y</sub>Al<sub>y</sub>)<sub>1-x</sub>O<sub>1-3x</sub>, as discussed above. Furthermore, after 2 h of calcination at 950 °C, Fe1Al1 OC was formed, composed of separate phases of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. This observation supported the earlier conclusion that calcination was the necessary procedure to avoid the formation of spinel phase between the active oxide and support. Different from the synthesis of Fe1Al1 OC, the separate phases  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> or  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> can be directly formed even without calcination.

Furthermore, according to Eq. (1), the averaged crystalline sizes for both the formed Fe1Al1 and the two reference oxides were evaluated. The sizes for all the samples after calcination were increased than those only after ignition. Especially for Fe<sub>2</sub>O<sub>3</sub>ig, its crystalline size increased greatly from 27.2 to 107.3 nm, due to the coalescence of neighboring crystallites during calcination. However, the crystalline size of Al<sub>2</sub>O<sub>3</sub>ig only increased a little from 63.9 to 73.2 nm. This proved the good resistance of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> to sintering and thus it can be used as the inert support for OC synthesis. Furthermore, the averaged crystalline sizes for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> present in the Fe1Al1si were correspondingly 37.6 and 67.8 nm, lower than their separate counterparts in sizes of 107.3 and 79.1 nm. It was also pos-



Fig. 6. X-ray diffraction patterns of the ignited and calcined Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> OC.



Fig. 7. Structural characteristics of the synthesized phases using SGCS: (a) N<sub>2</sub> adsorption-desorption isotherms; (b) pore size distribution; in which, ig and Si representing the synthesized products subjected to ignition and calcinations, respectively.

sibly due to the aluminum substitution during the formation of sol and the ensuing partial reciprocal solubility between  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> [26].

Finally, it was worthy to note that even though the calcination process was identified as a necessary step for the synthesis of Fe1Al1 OC, the calcination temperature in this research was 950 °C, which was still lower than all the other different preparation methods of Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> particles [26,27,44].

#### 3.4. Structure analysis of the synthesized Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> OC

As the oxygen carrier, the  $Fe_2O_3/Al_2O_3$  particle served as the reactant in CLC and the associated redox reactions were bulk reactions instead of a surface reaction like being used as a catalyst. Therefore, besides surface area, the pore size distribution is also important for the reactivity of OC [45]. N<sub>2</sub> adsorption analyzer was thus adopted to make a comprehensive characterization of both

the formed Fe1Al1 OC and the separate phase of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> synthesized using SGCS. The results are listed in Table 2. The isotherms and pore size distribution for Fe1Al1ig and Fe1Al1si are depicted in Fig. 7a and b, respectively. Meanwhile, these characteristics for the homemade  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>si and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>si were also provided for reference, respectively.

From Fig. 7(a), the hysteresis loops of the homemade Fe1Al1 OC and separate phases of Fe<sub>2</sub>O<sub>3</sub>Si and Al<sub>2</sub>O<sub>3</sub>Si were all different from the four typical hysteresis loops provided by International Union of Pure and Applied Chemistry (IUPAC). Below the relative pressure  $P/P_0 = 0.6$ , the adsorption branch increased slowly with the relative pressure and then intersected but not overlapped with the desorption branch, far different from all those four typical hysteresis loops nominated by IUPAC. Whereas above  $P/P_0 = 0.6$ , the adsorption branch did not reach the stable status even when  $P/P_0 = 1.0$ , much resembling that part of the H1 hysteresis loop at the larger relative pressure. Therefore, their



**Fig. 8.** Non-isothermal reduction of different oxides with  $H_2$ : (a) as-burned and calcined  $Fe_2O_3/Al_2O_3$  OC synthesized by SGCS; (b) the separate phases of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> from different sources.

Fable 2           Structural information of the Fe <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> OC and other separate reference phases synthesized by SGCS.					
Species	BET surface area (m <sup>2</sup> /g)	Single point porosity (cm <sup>3</sup> /g) (P/P <sub>0</sub> $\sim$ 0.97)	Average pore size (nm		
Fe <sub>2</sub> O <sub>3</sub>					
Ig <sup>a</sup>	1.4699	0.003438	3.6638		
Si <sup>a</sup>	0.6823	0.001390	9.3567		
Fe1Al1					
Ig <sup>a</sup>	12.1587	0.017442	5.7427		
Si <sup>a</sup>	1.6577	0.003327	8.0744		
$Al_2O_3$					

<sup>a</sup> Ig and Si denoting the products formed after the ignited and calcined processes by SGCS procedure, respectively.

0.006665

0.005245

pore types were more complicated and regarded as "heterogeneous", which were composed of several typical hysteresis loops [46]. The complexity of the pore shape was supposedly resulting from the preparation process using SGCS, in which, when NH<sub>4</sub>NO<sub>3</sub> was formed and present as oxidizer as shown in Eq. (3), a bigger amount of gases and a more violent reaction between urea and ammonia nitrate during the synthesis might complicated the pore shape [47].

16.0804

4 8 8 7 1

Iga Sia

Furthermore, from the pore size distribution of various samples depicted in Fig. 7(b), most of the pores for Fe1Al1ig were mesopore within 2-50 nm. When it underwent 2 h of calcination and formed into Fe1Al1si, many mesopores in Fe1Al1ig increased in size and transformed to macropore (>50 nm) due to the agglomeration and compaction of various neighboring mesopores. As references, the pore size distribution of the homemade separate phases, including  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>si and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>si were analyzed. The pores inside the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>si particle were mainly macropore bigger than 50 nm, but for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>si, even experiencing serious calcination, most pores were smaller than 50 nm, with two peaks occurring around 10 and 20 nm, respectively.

Finally, in Table 2, it was found that for all the oxides synthesized using SGCS, due to the sintering effect after calcination, the values of BET surface area, single porosity and fractal dimension decreased, but average pore size increased. And furthermore, all the values of Fe1Al1ig and Fe1Al1si fell between those of the synthesized separate phases, including Fe<sub>2</sub>O<sub>3</sub>ig, Al<sub>2</sub>O<sub>3</sub>ig and Fe<sub>2</sub>O<sub>3</sub>si, Al<sub>2</sub>O<sub>3</sub>si, potentially arising from the corresponding contribution of inert support Al<sub>2</sub>O<sub>3</sub>ig and Al<sub>2</sub>O<sub>3</sub>si.



Fig. 9. Four times of reduction and oxidization reactions (redox) between assintered Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> OC and alternate H<sub>2</sub> or air, respectively: (a) mass loss (TG) for the reactions; (b) mass loss rate (DTG) for the reactions.

#### 3.5. Reaction characteristics of the synthesized $Fe_2O_3/Al_2O_3$ OC

4.3845

7 2665

#### 3.5.1. $H_2$ -TPR of the Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> OC

In relative to the oxidation reaction of the reduced OC in AR. reduction reaction of the OC with fuel in FR is generally considered as the limiting step. Gaseous fuels such as CH<sub>4</sub> or CO easily generated carbon deposition and caused the reduction reaction complicated. Therefore, to get a preliminary understanding of the reaction characteristics of the synthesized Fe1Al1 OC, the reduction reaction with H<sub>2</sub> was performed in TGA. The results are depicted in Fig. 8a. As the reference, the reduction reactions of separate active phase  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> produced by SGCS with the same procedure along with two commercial  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> oxides, designated as  $Fe_2O_3ig$ ,  $Fe_2O_3si$ ,  $Fe_2O_3(R)$  and  $Fe_2O_3(M)$ , respectively, are provided in Fig. 8b for a comparison. Here, R and M in the brackets represented the commercial oxides ordered from Riedel-dehaen and Merck Corporations.

According to Fig. 8a, there existed three distinct DTG peaks in the reduction reaction of as-burnt Fe1Al1ig, which were centered at 384.43, 405.26 and 813.20 °C, accompanying with the left mass from the TG curve to reach 98.19%, 90.92% and 83.16%, respectively. According to the above IR analysis and phase identification, Fe1Al1ig was composed of FeAl<sub>2</sub>O<sub>4</sub> and α-Fe<sub>2</sub>O<sub>3</sub>. Reasonably supposing the complete reaction of both FeAl<sub>2</sub>O<sub>4</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with H<sub>2</sub> [48–50], the mass fraction of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> present in Fe1Al1(ig) was calculated as 53.92% through the net mass loss (100-90.92% = 9.08%) for the reduction of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with H<sub>2</sub> to divide the total net loss (100-83.16% = 16.84%) for the complete reduction of Fe1Al1ig with H<sub>2</sub>. Furthermore, the following three reactions could be inferred. Firstly, at the range of 253–411 °C,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> reacted with H<sub>2</sub> into Fe<sub>3</sub>O<sub>4</sub> with 98.19% left. And then at 411-611 °C, Fe<sub>3</sub>O<sub>4</sub> completely reacted into Fe with 90.92% left. Finally, with temperature increasing upward from 611 °C, the reduction reaction of Fe1Al1<sub>2</sub>O<sub>4</sub> proceeded until terminated at 915 °C with 83.20% left. Therefore,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> present in Fe1Al1ig reacting with H<sub>2</sub> experienced two reaction steps from  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> into Fe<sub>3</sub>O<sub>4</sub> and further into Fe, which was consistent with the previous observations [48,49]. After that, FeAl<sub>2</sub>O<sub>4</sub> reacted with H<sub>2</sub> into Fe and Al<sub>2</sub>O<sub>3</sub> [50]. Different from the reaction of Fe1Al1ig with H<sub>2</sub>, there was only one DTG peak centering at 506.45 °C for the reduction reaction of Fe1Al1Si with H<sub>2</sub>, which consisted of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as above mentioned. This sole peak implied the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> present in Fe1Al1Si OC directly reacted with H<sub>2</sub> into Fe at the temperature range of 351–623 °C, and single step reaction was involved.

Furthermore, the mass loss in TG curve for both Fe1Al1ig and Fe1Al1Si reacting with H<sub>2</sub> was actually resulting from the loss of lattice oxygen present in the oxide carrier. Accordingly, the DTG value implied the transfer rate of the lattice oxygen in the oxides to H<sub>2</sub>: a bigger DTG value meant a larger transfer rate. In Fig. 8a. the DTG value for Fe1Al1Si was 1.42%/°C, far bigger than any DTG values of the three sequential reactions involved for Fe1Al1ig react-

Fractal dimension

2.68 2.45

2 91 2.75

2.94

2 88



Fig. 10. SEM images of Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> OC: (a) as-synthesized Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> OC; (b) Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> OC after four cycles of redox reactions.

ing with H<sub>2</sub>, which meant Fe1Al1Si had a greater oxygen transfer rate and was more suitable for CLC application, because when OC was used in CLC system, higher oxygen transfer rate meant less bed inventory in FR and less recirculation of OC from AR to FR [51].

Finally, in Fig. 8b, there were two distinct DTG peaks for the reduction reaction of each commercial  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with H<sub>2</sub>, which was similarly ascribed to the reduction of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> into Fe<sub>3</sub>O<sub>4</sub> and Fe with double-step reactions. On the contrary, the homemade  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> using SGCS had only one DTG peak and single reduction reaction of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> directly into Fe was involved. Furthermore, the DTG values for the two homemade  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (both Fe<sub>2</sub>O<sub>3</sub>ig and Fe<sub>2</sub>O<sub>3</sub>si) were far bigger than those of the commercial oxides; therefore, these oxides produced using SGCS had a greater oxygen transfer rate and could be more suitable for CLC application.

#### 3.5.2. Redox process of the $Fe_2O_3/Al_2O_3$ OC with $H_2$ and air

Good redox properties and sintering-resistance are of the great concerns to sustain the good reactivity of the oxygen carrier adopted in CLC. In order to evaluate redox and the sinteringresistant characteristics for the as-synthesized Fe1Al1 OC, four cyclic times of reducing and oxidizing reactions between assintered Fe1Al1 OC and alternating by  $H_2$  in 50 vol% with balance  $N_2$  and then air were performed using TGA (TA 2050, US). The result of mass loss (i.e., TG curve) and those of the corresponding differential mass loss rate (i.e., DTG curve) over the four times of redox process are plotted in Fig. 9a and b, respectively.

From Fig. 9, it was observed that though the first redox reaction rates with H<sub>2</sub> and air were corresponding to 8.2%/min and 41.8%/min, but with the reaction further proceeding, the rates related to the reduction by H<sub>2</sub> and oxidization by air were increased greatly, stabilizing around 20%/min and 50%/min, respectively. The lower reduction rate for the first cycle was mainly arising from the dense layer Fe<sub>2</sub>O<sub>3</sub> initially formed in the outer surface and the uneven pore size distribution for the fresh Fe1Al1 OC during preparation (as seen in Fig. 10a). Both the dense layer formed outside the OC particle and the uneven pore size distribution prevent H<sub>2</sub> to access the active reaction surface, which was in agreement with the observation by other researchers [52-54]. But after the first redox process, the abundant pores of different size were developed over the ensuing redox process by enlargement in the reduction stage and contraction in the oxidization stage with the variation in the molar volume of reduction product Fe and oxidization product Fe<sub>2</sub>O<sub>3</sub>, which was greatly beneficial to increase the reaction rates. Furthermore, the stable redox rates after the first redox process and the rich pore distribution (as seen in Fig. 10b) demonstrated the synthesized Fe1Al1 OC possessed good sintering-resistance, which was important to sustain the reactivity over many times of redox processes in the realistic CLC.

#### 4. Conclusions

In combination of sol-gel route and solution combustion synthesis, a novel synthesis method of oxygen carrier (named SGCS) was first put forward and systematically studied, to develop new oxygen carriers with improved performance to be used in CLC. The detailed preparation procedure was designed and various parameters involved in SGCS were discussed. The reaction performance of  $Fe_2O_3/Al_2O_3$  OC in fuel reactor was further preliminarily studied. Comprehensive investigations of  $Fe_2O_3/Al_2O_3$  OC synthesized using SGCS proved that it was more advantageous than the reported preparation methods. The characterization of the  $Fe_2O_3/Al_2O_3$  OC synthesized by SGCS was focused in this study. The conclusions were reached as follows:

- (i) The chemical structure of the dried gel of Fe1Al1 OC was analyzed using FTIR. In the evolution of urea, part of urea hydrolyzed and various ions including  $NH^{4+}$ ,  $NCO^{-}$  and  $CO_3^{2-}$ were produced. The ions of  $Fe^{3+}$  and  $Al^{3+}$  were complexed with OH group and  $CO_3^{2-}$ , and thus the complicated hydrated basic carbonate was formed. Further analysis of the staged Fe1Al1 products after ignition and continual calcination proved that calcination was a necessary step to produce Fe1Al1 OC with separate phases of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, possibly due to the occurrence of aluminum substitution in the formed complex.
- (ii) The thermal decomposition of the dried gel was found to undergo five different stages, including the two endothermic thermal dehydrations in sequence and the ensuing decomposition of carbonate, exothermic combustion reaction between urea and ammonia nitrates along with the final phase transformation of the formed oxides. Furthermore, the evolved gases were ascertained by FTIR coupled with TGA, showing less N<sub>2</sub>O and NH<sub>3</sub> were produced than the traditional combustion synthesis due to the postponement of the decomposition of ammonium nitrate with the presence of urea and the exothermic reaction between NH<sub>3</sub> and NO<sub>x</sub>.
- (iii) XRD identification of the various products for Fe1Al1 formed by SGCS further verified that calcination was necessary to obtain Fe1Al1 OC with separate phases, similar to that reached through FTIR analysis. But for the synthesis of single phase  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, the ignition at 600 °C for 15 min sufficed without further calcination.
- (iv) Structural characterization indicated that the pore shape of Fe1Al1 composite particles using SGCS was heterogeneous and the pore size mainly fell in mesopore after calcination due to sintering.
- (v) Finally, H<sub>2</sub> TPR of Fe1Al1 products in TGA indicated that the reduction reaction of Fe1Al1 OC after calcination was a single

reaction from  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> to Fe, though the reactions of Fe1Al1ig only after ignition were triple steps of reactions. And calcination benefited to improve the transfer rate of the lattice oxygen from the OC to fuel H<sub>2</sub>. Furthermore, four times of redox reaction by alternating with H<sub>2</sub> or air demonstrated the synthesized OC had good reactivity and sintering-resistance, more beneficial to be used in the realistic CLC.

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