Isomorphous Replacement in Fe₂O₃–NiO/Al₂O₃ Particles and Its Effect on Oxygen Carrier Performance

Qindong Chen¹, Song Hu^{1, 2*}, Jun Xiang^{1, 2}, Sheng Su^{1, 2}, Lushi Sun^{1, 2}, Yi Wang¹,
Liangpin Zhang¹, Huanying Chi²

¹State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074

²Institute for Clean and Renewable Energy, Huazhong University of Science and Technology, Wuhan 430074

ABSTRACT

Using Fe₂O₃, Fe₂O₃/Al₂O₃, and Fe₂O₃–NiO/Al₂O₃ as oxygen carriers (OCs) on chemical looping combustion with CO was investigated in this study. All the modified iron-based OCs were prepared by sol–gel method, and the samples were characterized by X-ray diffraction (XRD), N₂ adsorption/desorption, and scanning electron microscope/energy dispersive X-ray spectroscopy. The temperature-programmed reduction showed that loading on Al₂O₃ will promote the reduction of Fe₂O₃ to Fe₃O₄, but further reduction will be inhibited, and the addition of NiO can effectively reduce this inhibition. Thermogravimetric analysis also revealed that NiO addition can improve the maximum reaction rate of iron-based OCs in the oxidation stage. Mixing with NiO will also decrease the oxygen capacity of iron-based OCs. The XRD data of the reduced samples showed that both Al₂O₃ and NiO have an isomorphous replacement effect on Fe₃O₄. The isomorphous replacement effect of NiO is much

*Corresponding author: Song Hu, email: husong_hust@hotmail.com; Tel.: +86-27-87542417; Fax: +86-27-87545526.

stronger than that of Al_2O_3 . Thus, NiO introduction can effectively inhibit the formation of FeAl_2O_4 and promote the further reduction of Fe-oxides to Fe. However, Ni^{2+} will replace part of the Fe^{2+} in Fe_3O_4 to form NiFe_2O_4 and slightly decrease the oxygen capacity of iron-based OCs.

Keywords: Iron oxide, Chemical looping, Carbon monoxide, NiO, Isomorphous replacement

1. Introduction

Chemical looping combustion (CLC) technology is a newly developing technology which can realize the inherent separation of CO_2 due to its special reaction way, and oxygen carrier (OC) is a key role for sustainable reaction of CLC [1]. Iron-based oxygen carriers are good candidates for CLC because most of them (pure Fe_2O_3 and iron ores) possess high mass fraction of oxygen and high melting point, and are inexpensive as well as environmentally sound [1-3]. However, compared with other OCs, such as CuO and NiO, Fe_2O_3 reactivity is still relatively low; the reaction temperature needed is also higher, and the higher reaction temperature of Fe_2O_3 makes it easily sintered during the CLC process [2,4,5]. In addition, the mechanical strength of pure Fe_2O_3 is insufficient for the continuous CLC process [3]. Thus, a series of modifications on iron-based OCs are carried out to promote their comprehensive ability [6,7].

Loading pure OCs on inert mediums, e.g., Al_2O_3 , ZrO, or SiC, is a common method to improve their mechanical strength and subsequently increase their

regeneration capacities; samples prepared via sol–gel method are assumed to be much stable when compared with other samples prepared through other methods, such as mechanical mixing, impregnation, dissolution, and co-precipitation [6-8]. Kierzkowska et al. [6] found that during the CLC process with CO/H₂O as the reduction atmosphere, the supported Fe₂O₃ with 40 wt% Al₂O₃ can result in a stable H₂ conversion of 75% for over 40 cycles, whereas that of unsupported Fe₂O₃ drops to 3% after 10 cycles. Wang et al. [7] also found that iron-based OCs with Fe: Al=1:1 possess stable oxygen capacity of about 76% for the CLC process, with H₂ as the reducing environment. Similarly, OC reactivity can be promoted by mixing with other compounds. Moghtaderi et al. [9] found that the kinetic parameters of physically mixed binary mixtures of CuO/Fe₂O₃ and NiO/Fe₂O₃ are improved. They also found that a mixture of Ni- and Fe-based metal oxides can be as effective but less toxic and cheaper than its parent materials [9,10].

However, iron-based OC loading on Al₂O₃ make it difficult to achieve full conversion to Fe [2,7,11]; specifically, the maximum oxygen capacity cannot reach 100%, and even decreases if the Al₂O₃ amount increases [6]. Bhavsar et al. [10] also found that the introduction of NiO in Fe–Al₂O₃ (Fe: Ni=2.21) will decrease its maximum oxygen capacity by approximately 6.5%. Moghtaderi et al. [9] simply ascribed the reactivity improvement of CuO/Fe₂O₃ to the increase in specific surface area of the sample. Obviously, the mechanism for improving metal oxide addition is still unclear.

It is significant for improving OC modification to understand the interaction

among the compounds of OC particles. Iron can be isomorphically replaced in magnetite Fe_3O_4 by other metals (mainly transition metals) in crystal chemistry studies [12-14]; such phenomenon is called isomorphous replacement, which will significantly change several physicochemical properties of the material [15]. Furthermore, isomorphous replacement is assumed to occur in OC particles, thereby leading to their changed reaction behaviors during the CLC process, e.g., decrease in oxygen capacity.

In the current work, Fe_2O_3 , $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, and $\text{Fe}_2\text{O}_3\text{--NiO}/\text{Al}_2\text{O}_3$ were selected to study the interaction among compounds during CO-CLC reaction. The reaction behavior of OCs was investigated using a thermogravimetric analysis (TGA) reactor with CO/air atmosphere. The samples before and after reaction were characterized to analyze the crystal structure of the particles and determine an evidence for isomorphous replacement. The influence of isomorphous replacement on the reaction behavior of iron-based OCs is further discussed.

2. Experimental

2.1. OC preparation

In this study, Fe_2O_3 was used as the parent OC, and pure Fe_2O_3 was prepared by calcining $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sinopharm Chemical Reagent Co., Ltd., China 99%) at 950 °C in air atmosphere for 6 h in a muffle furnace.

Modified iron-based OCs ($\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3\text{--NiO}/\text{Al}_2\text{O}_3$) were prepared via the sol–gel method. Typically, aluminum isopropoxide (Sinopharm Chemical Reagent Co., Ltd., 98%) was first hydrolyzed in distilled water with an oil bath heating at

about 80 °C for 2 h. Nitric acid (1 mol/L) was then added to generate aluminum nitrate by reacting with aluminum hydroxide, and boehmite sol was obtained. Finally, the dissolved aqueous solution of $\text{Fe}(\text{NO}_3)_3$ or the mixture aqueous solution of $\text{Fe}(\text{NO}_3)_3$ and $\text{Ni}(\text{NO}_3)_2$ was added into the boehmite sol under continuous stirring at 75 °C for 1 h. The resulting production was calcined at 950 °C for 6 h in air atmosphere.

For the modified OCs, the ratio of Fe to Al_2O_3 is 2:1, and the ratio of Fe to Ni is 10:1. It should be noted that all the ratios mentioned in this work are molar ratios.

2.2. OC characterization

X-ray diffraction (XRD) analyses were conducted to study the chemical structure of the OC samples by using an X-ray diffractometer (PANalytical B.V. X'Pert-Pro) with a Cu $K\alpha$ monochromatized radiation source and a Ni filter within the range of $2\theta=10^\circ\text{--}90^\circ$. Temperature-programmed reduction (TPR) analyses were performed to evaluate the reduction property of the OCs. Next, 50 mg of OC was subjected to the TPR measurement, and pretreatment was carried out at 300 °C (25 °C/min) in the pure Ar gas flow (40 mL/min) and cold down to 200 °C; the analysis was proceeded with heating rate (10 °C/min) in a gas flow (40 mL/min) containing a mixture of H_2 : Ar (10:90). The change in H_2 content during the reduction was measured using a thermal conductivity detector. N_2 adsorption/desorption analysis was carried out at -196°C by using an automated gas adsorption analyzer (Micromeritics ASAP2020). The morphology of the samples was characterized by using a scanning electron microscope (SEM, Tescan, VEGA/SBU) equipped with energy dispersive X-ray

spectroscopy (EDX, Oxford, OXFORD/Inc a-X-Max-20). Both SEM and BET analyses were used to study the physical structure of the OC samples and all the reacted samples were prepared on the fixed bed reactor.

2.3. Redox performance of OCs

According to the suggestion of references [16], the five cycles' redox reaction was performed in thermogravimetric analysis (TGA, Netzsch, STA449F3) to evaluate oxygen carrier performance. Specific steps were as follows: (1) 10 ± 0.5 mg of the prepared OC with sizes under 200 μm was charged in the reactor; (2) the samples were heated to 900 $^{\circ}\text{C}$ at an oxidation atmosphere (21% O_2 and 79% N_2) with a heating rate of 50 $^{\circ}\text{C}/\text{min}$ and then kept constant temperature till the end of the test; (3) The gas flow was switched to the reduction gas for 1 h when the temperature kept at 900 $^{\circ}\text{C}$; (4) After the reduction reaction, the gas was turned back to air for 15 min for OC regeneration. (5) Repeat steps (3) and (4) for five times. In this experiment, the feed gas for reduction contained 10% CO and 90% N_2 with a gas flow of 100 mL/min, and air was used for oxidation with 100 mL/min.

3. Results And Discussion

3.1. Redox cycle performance of the OCs

Five cycles of the redox reaction of OCs were conducted through TGA to study their reactivity and regeneration capacities. The conversion capacity of OCs is defined as follows:

$$X = \Delta m / \sum C_i C_{i0}$$

Where X is the conversion capacity of the OC (%), Δm is the mass loss of the sample

(%), C_i is the mass fraction of active component i in the OC, and C_{iO} is the mass fraction of oxygen element in the active component i .

The conversion rate R is defined as follows:

$$R = dX/dt$$

Fig. 1 shows the calculated results. All the modified OC samples suffered low conversion capacity in the first redox cycle, which was mainly caused by the dense Fe_2O_3 layer initially formed in the outer surface of the fresh samples; moreover, the maximum conversion capacity will keep increasing in the first few cycles [7,17,18], and it will get stable after a few cycles. To reduce the influence of the dense layer, the last three cycles were selected to study the decay status of the OCs during redox cycle reaction. Table 1 shows the maximum X (X_{max}) and R (R_{max}) at each reduction stage of the OCs.

Fe_2O_3 achieves the largest conversion capacity at the first cycle (93.67%), and the performance of Fe_2O_3/Al_2O_3 is the best after five cycles (92.36%) (Fig. 1). All the iron-based OCs cannot achieve full conversion in the reaction. For modified OCs, obtaining 100% conversion is difficult mainly because the lower valence Fe-oxide may combine with Al_2O_3 to form $FeAl_2O_4$ [19,20], which is very difficult to be reduced further. Additionally, the X_{max} of Fe_2O_3-NiO/Al_2O_3 is lower than that of Fe_2O_3/Al_2O_3 at all cycles. These properties of modified OCs will be discussed in the next section. Al_2O_3 and NiO addition can also effectively improve the reactivity of iron-based OCs according to Table 1. After five cycles of redox reaction, the average maximum conversion rates at the reduction [$R_{max}(Re)$] and oxidation [$R_{max}(Ox)$]

stages of $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ are 5.2 and 2.5 times more than that of the pure Fe_2O_3 respectively. The addition of NiO to $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ also increases these rates by 5.4 and 2.4 times respectively.

3.2. Characteristic of iron-based OCs

3.2.1. Physical structure of OCs

Fig. 2 shows the N_2 adsorption/desorption isotherm results of the fresh iron-based OCs, and their structural properties are listed in Table 2. The BET surface areas of the samples are of the same order and do not show obvious difference. According to the IUPAC classification, the isotherms of OCs can be classified as a V isotherm [Fig. 2(a)]. The hysteresis loop shapes of the OCs are mixtures of types H1 and H3. The type H1 hysteresis reflects the mesoporous materials [21], and the type H3 hysteresis is characteristic of solids having slit-shaped pores, which mainly composed of plate-like particles or a layer structure [22].

Fig. 2(b) displays the pore size distribution curves calculated from the desorption branch of the isotherms. The figure indicates that the pore sizes of OCs are mainly within the range of 1–5 nm and 30–100 nm. $\text{Fe}_2\text{O}_3\text{--NiO}/\text{Al}_2\text{O}_3$ contains a similar amount of macropores as Fe_2O_3 and $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, but its micropores (<3 nm) are almost disappearing. This outcome mainly attributes to the pore structures of $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ being blocked by the smaller molecule NiO. Their specific surface areas do not have a significant change (Table 2), and thus the physical structures of these OCs do not have obvious effects on reactivity changes.

Fig. 3 shows the SEM images of the OC samples before and after five redox

cycles. Corresponding to the N_2 adsorption/desorption results, Fig. 3 shows that Fe_2O_3 –NiO/ Al_2O_3 is considerably more compact. The loose particle structure means a low mechanical strength [23], even though the pure Fe_2O_3 sample shows a much complicated and loose surface condition. Fig. 3(e) shows that pure Fe_2O_3 is sintered after reaction, and the modified samples show better heat-resistant property than the pure Fe_2O_3 . Moreover, Fe_2O_3 / Al_2O_3 samples [Fig. 3(f)] are cracked after reaction, whereas Fe_2O_3 –NiO/ Al_2O_3 [Fig. 3(g)] still keeps the complete particles to show its excellent thermal mechanical strength.

3.2.2. TPR characteristic of OCs

To further study the reduction behavior of the iron-based OCs, H_2 –TPR analysis was performed. Fig. 4 displays the TPR results of all samples. The first peak occurs at about 450 °C–500 °C, which attributes to the reduction of Fe_2O_3 to Fe_3O_4 [24]. The first peak of Fe_2O_3 / Al_2O_3 and Fe_2O_3 –NiO/ Al_2O_3 shift to the lower temperatures (ΔT_1 in Fig. 4, ~50 °C). This result indicates that a sample modification can promote Fe_2O_3 reduction because loading Fe_2O_3 on Al_2O_3 decreases the reaction energy barrier for CO oxidation (from 2.59 eV to 1.08 eV) [25]. The second peak which shows at about 550 to 850 °C represents the transformations of $Fe_3O_4 \rightarrow FeO \rightarrow Fe$. However, the second peak of Fe_2O_3 / Al_2O_3 and Fe_2O_3 –NiO/ Al_2O_3 , shift to the higher temperatures (ΔT_2 in Fig. 4, ~55 °C) due to the formation of $FeAl_2O_4$ [20]. In addition, $\Delta T_2'$ (Fe_2O_3 –NiO/ Al_2O_3) is much smaller than ΔT_2 (Fe_2O_3 / Al_2O_3), which means NiO addition inhibits the generation of $FeAl_2O_4$.

3.3. Crystal structure and isomorphous replacement of the iron-based OCs

XRD analysis was performed to study the crystallite phases in the samples. Fig. 5(a) shows the XRD patterns of pure Fe_2O_3 and modified iron-based OCs. The XRD patterns of Fe_2O_3 show a rhombohedral Fe_2O_3 crystal structure (JCPDS PDF 00-033-0664). A cubic crystal structure is shown by $\text{Al}_3\text{Fe}_5\text{O}_{12}$ (JCPDS PDF 00-049-1657) in the modified samples, with peaks assigned to the $\text{Al}_3\text{Fe}_5\text{O}_{12}$ (332) and (431) at around $2\theta = 33.5^\circ$ and 36.0° . These peaks overlap with the peaks of Fe_2O_3 . Furthermore, no diffraction peak of NiO in the XRD results indicates that NiO is highly dispersed in the samples. The EDX surface scan result in Table 3 shows that the molar ratio of Ni:Fe on the surface of the particles is near to 1:10, which is the theoretical component molar ratio of the samples and indicates that the Ni- particles are bulk distributed evenly in the OC particles.

Fig. 5(b) shows the XRD patterns of the OCs after one reduction reaction. Only one cubic crystal (JCPDS PDF 01-087-0722) is observed in the Fe_2O_3 XRD pattern. To combine the XRD result [Fig. 5(b)] with $X_{\max}$ (Table 1), the unreduced Fe- oxides should be surrounded by Fe crystals. Consequently, no peaks for other compounds are shown in the XRD pattern. The modified OCs shows the much complicated phenomenon. The FeAl_2O_4 crystal (JCPDS PDF 01-086-2320) is observed in $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, and its diffraction peaks (400) overlap with those of Fe (110) at about $2\theta = 44.4$. No FeAl_2O_4 , but NiFe_2O_4 (JCPDS PDF 01-086-2267), is found in $\text{Fe}_2\text{O}_3\text{-NiO}/\text{Al}_2\text{O}_3$. Its diffraction peaks (400) overlap with those of Al_2O_3 (113) at about $2\theta = 43.4$.

No Ni in the fresh OCs indicates that NiFe_2O_4 crystals generate during reduction

reaction. Furthermore, all metal elements in this crystal are at their highest valence state, and thus these crystals are probably not produced by reacting with lower valence Fe-oxides but are generated by replacing the molecules in other crystals, a process called isomorphous replacement [Fig. 5(a)]. FeAl_2O_4 and NiFe_2O_4 show similar cubic crystal parameters with Fe_3O_4 (point group: $m\bar{3}m$); both are produced when Fe^{2+} or Fe^{3+} in Fe_3O_4 crystal particles are replaced by Ni^{2+} and Al^{3+} respectively [13].

3.4. Isomorphous replacement effect on the iron-based OCs

In a stoichiometric magnetite Fe_3O_4 , all Fe^{2+} ions typically occupy octahedral positions (B sites), whereas Fe^{3+} ions are distributed equally between tetrahedral (A) and octahedral (B) sites [13]. Fe replacement by Al and Ni occurs only in B sites [14]. The replacement of transition metal will also make the crystal structure much more stable [26]. These isomorphous replacement processes can be expressed in the following equations:

To better study the reaction process of iron-based OCs, the thermodynamic equilibrium as a function of the CO amount fed to the system based on the minimum Gibbs free energy principle was calculated, and the results are shown in Fig. 6. The reaction was carried out at 900 °C and 1 bar, the initial amount of Fe_2O_3 is 10 moles and NiO is 2 moles. It is easy to notice that NiO begins to reduce only after Fe_2O_3 fully converts to Fe_3O_4 , which verifies the possibility of an isomorphous replacement

[Fig. 6(b)].

To sum up, NiO has stronger isomorphous replacement ability for Fe_3O_4 than for Al_2O_3 , so the introduction of NiO can effectively inhibit the formation of FeAl_2O_4 . During the isomorphous replacement process, Al^{3+} replaces Fe^{3+} and releases a more active substance (Fe_2O_3), whereas Ni^{2+} replaces Fe^{2+} and releases FeO (Fig. 7). NiO is the active compound, and thus Ni replacement will decrease the oxygen capacity of iron-based OCs. This inference conforms to the TGA result (Fig. 1) that Fe^{2+} replacement by Ni^{2+} can accelerate FeO generation. This replacement can also improve the reduction process of Fe-oxides to Fe, consistent with the results in the TPR analysis (the peaks at about 900 °C in Fig. 4).

4. Conclusion

This study on modified iron-based OCs obtained the following results.

- 1) All the modified iron-based OCs show better reactivity and stability during reaction, and NiO addition can further improve their thermal mechanical strength.
- 2) Isomorphous replacement is observed in $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3\text{-NiO}/\text{Al}_2\text{O}_3$ during reaction according to the XRD analysis and thermodynamic equilibrium calculation results.
- 3) Isomorphous replacement of Al_2O_3 on Fe_3O_4 will inhibit the further reduction of Fe-oxides. NiO addition can effectively inhibit the isomorphous replacement effect of Al_2O_3 , and the isomorphous replacement of NiO on Fe_3O_4 can promote further reduction of Fe-oxides as well as slightly

decrease the oxygen capacity of iron-based OCs.

Acknowledgement

This project is supported by the National Science Foundation of China (NSFC) (NO. 51176062, No. 51576081), the Research Project of Chinese Ministry of Education (NO. 20130142110086), Program for New Century Excellent Talents in University (NCET-13-0226), Hubei Natural Science Funds for Distinguished Young Scholar (NO. 2013CFA036), and the Foundation of State Key Laboratory of Coal Combustion (NO.FSKLCCB1404). The authors are grateful to the Analytical and Testing Center of Huazhong University of Science and Technology.

Nomenclature

BET = Brunner–Emmet–Teller measurements

CLC = chemical looping combustion

EDX = energy dispersive X-ray spectroscopy

OC = oxygen carrier

Ox= oxidation

Re= reduction

SEM = scanning electron microscope

TGA = thermogravimetric analysis

TPR = temperature-programmed reduction

XRD = X-ray diffraction

References:

[1]. Ryden, M., E. Cleverstam, M. Johansson, A. Lyngfelt, and T. Mattisson, Fe₂O₃

- on Ce-, Ca-, or Mg-Stabilized ZrO_2 as Oxygen Carrier for Chemical-Looping Combustion Using NiO as Additive. *AIChE Journal*, 56 (2010) 2211-2220.
- [2]. Chiu, P.C., Y. Ku, Y.L. Wu, H.C. Wu, Y.L. Kuo, and Y.H. Tseng, Characterization and evaluation of prepared $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ oxygen carriers for chemical looping process. *Aerosol and Air Quality Research*, 14 (2014) 981-990.
- [3]. Mattisson, T., A. Lyngfelt and P. Cho, The use of iron oxide as an oxygen carrier in chemical-looping combustion of methane with inherent separation of CO_2 . *Fuel*, 80 (2001) 1953-1962.
- [4]. Adanez-Rubio, I., A. Abad, P. Gayan, L.F. de Diego, F. Garcia-Labiano, and J. Adanez, Biomass combustion with CO_2 capture by chemical looping with oxygen uncoupling (CLOU). *Fuel Processing Technology*, 124 (2014) 104-114.
- [5]. Takayuki Takarada, Y.T.A.T., Reactivities of 34 coals under steam gasification. *Fuel*, 10 (1985) 1438-1442.
- [6]. Kierzkowska, A.M., C.D. Bohn, S.A. Scott, J.P. Cleeton, J.S. Dennis, and C.R. Muller, Development of iron oxide carriers for chemical looping combustion using Sol-Gel. *Industrial & Engineering Chemistry Research*, 49 (2010) 5383-5391.
- [7]. Wang, B.W., R. Yan, D.H. Lee, Y. Zheng, H.B. Zhao, and C.G. Zheng, Characterization and evaluation of $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ oxygen carrier prepared by sol-gel combustion synthesis. *Journal of Analytical and Applied Pyrolysis*, 91 (2011) 105-113.

- [8]. Mei, D.F., A. Abad, H.B. Zhao, and J. Adanez, Characterization of a sol-gel derived CuO/CuAl₂O₄ oxygen carrier for chemical looping combustion (CLC) of gaseous fuels: Relevance of gas-solid and oxygen uncoupling reactions. *Fuel Processing Technology*, 133 (2015) 210-219.
- [9]. Moghtaderi, B. and H. Song, Reduction properties of physically mixed metallic oxide oxygen carriers in chemical looping combustion. *Energy & Fuels*, 24 (2010) 5359-5368.
- [10]. Bhavsar, S. and G. Veser, Bimetallic Fe-Ni oxygen carriers for chemical looping combustion. *Industrial & Engineering Chemistry Research*, 52 (2013) 15342-15352.
- [11]. Wei, G.Q., F. He, Z. Huang, K. Zhao, A.Q. Zheng, and H.B. Li, Chemical-Looping reforming of methane using iron based oxygen carrier modified with low content nickel. *Chinese Journal of Chemistry*, 32 (2014) 1271-1280.
- [12]. Magalhaes, F., M.C. Pereira, S. Botrel, J.D. Fabris, W.A. Macedo, and R. Mendonca, et al., Cr-containing magnetites Fe_{3-x}Cr_xO₄: The role of Cr³⁺ and Fe²⁺ on the stability and reactivity towards H₂O₂ reactions. *Applied Catalysis A-General*, 332 (2007) 115-123.
- [13]. Menini, L., M.C. Pereira, L.A. Parreira, J.D. Fabris, and E.V. Gusevskaya, Cobalt- and manganese-substituted ferrites as efficient single-site heterogeneous catalysts for aerobic oxidation of monoterpene alkenes under solvent-free conditions. *Journal of Catalysis*, 254 (2008) 355-364.

- [14]. Zhong, Y.H., X.L. Liang, W. Tan, Y. Zhong, H.P. He, and J.X. Zhu, et al., A comparative study about the effects of isomorphous substitution of transition metals (Ti, Cr, Mn, Co and Ni) on the UV/Fenton catalytic activity of magnetite. *Journal of Molecular Catalysis A-Chemical*, 372 (2013) 29-34.
- [15]. Labeguerie, P., M. Harb, I. Baraille, and M. Rerat, Structural, electronic, elastic, and piezoelectric properties of alpha-quartz and M_xO_4 ($M=Al, Ga, Fe$; $X=P, As$) isomorph compounds: A DFT study. *Physical Review B*, 81 (2010).
- [16]. P. GUPTA, Regenerable metal oxide composite particles and their use in novel chemical processes. The Ohio State University, (2006) p. p. 319.
- [17]. Zafar, Q., A. Abad, T. Mattisson, B. Gevert, and M. Strand, Reduction and oxidation kinetics of $Mn_3O_4/Mg-ZrO_2$ oxygen carrier particles for chemical-looping combustion. *Chemical Engineering Science*, 62 (2007) 6556-6567.
- [18]. Siriwardane, R., J. Poston, K. Chaudhari, A. Zinn, T. Simonyi, and C. Robinson, Chemical-looping combustion of simulated synthesis gas using nickel oxide oxygen carrier supported on bentonite. *Energy & Fuels*, 21 (2007) 1582-1591.
- [19]. Goncharov, O.Y., O.V. Karban, O.M. Nemtsova, and I.A. Il'In, Analysis of the formation of $Al_2O_3 + Fe$ nanocomposites. *Glass Physics and Chemistry*, 35 (2009) 210-218.
- [20]. Adanez, J., A. Abad, F. Garcia-Labiano, P. Gayan, and L.F. de Diego, Progress in Chemical-Looping Combustion and Reforming technologies. *Progress in Energy and Combustion Science*, 38 (2012) 215-282.

- [21]. Larese, C., J.M. Campos-Martin and J. Fierro, Alumina- and zirconia-alumina-loaded tin-platinum. Surface features and performance for butane dehydrogenation. *Langmuir*, 16 (2000) 10294-10300.
- [22]. Tsai, W.T., H.P. Chen, M.F. Hsieh, H.F. Sun, and S.F. Chien, Regeneration of spent bleaching earth by pyrolysis in a rotary furnace. *Journal of Analytical and Applied Pyrolysis*, 63 (2002) 157-170.
- [23]. Guo, H., H.L. Zhao and X.D. Ha, Spherical Sn-Ni-C alloy anode material with submicro/micro complex particle structure for lithium secondary batteries. *Electrochemistry Communications*, 9 (2007) 2207-2211.
- [24]. Biabani, A., M. Rezaei and Z. Fattah, Catalytic performance of Ag/Fe₂O₃ for the low temperature oxidation of carbon monoxide. *Chemical Engineering Journal*, 219 (2013) 124-130.
- [25]. Chen, Q.L., Density function study of Fe₂O₃ synergy with inser in Chemical-Looping combustion system. 2013, North China Electric Power University. p. 62.
- [26]. Huang, H., X. Zheng and Y.G. Chen, Iron oxides isomorphous substituted by transition metals and their application in heterogeneous fenton reaction. *Chemistry*, (2014) 1144-1150.

Figure captions

Fig. 1. Cycle performance of the OCs

Fig. 2. (a) N₂ adsorption/desorption isotherms of the the OCs, (b) pore diameter

distribution of the OCs (BJH model)

Fig. 3. SEM image of the OCs before ((a) Fe_2O_3 , (b) $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, (c)

$\text{Fe}_2\text{O}_3\text{-NiO}/\text{Al}_2\text{O}_3$) and after ((e) Fe_2O_3 , (f) $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, (g) $\text{Fe}_2\text{O}_3\text{-NiO}/\text{Al}_2\text{O}_3$)

reaction

Fig. 4. H_2 -TPR result of the OCs

Fig. 5. XRD patterns of the OCs before (a) and after (b) reduction reaction

Fig. 6. Thermodynamic equilibrium as a function of the CO amount fed to the system.

$T = 900\text{ }^\circ\text{C}$. $P = 1\text{ bar}$

Fig. 7. Reaction mechanism of the iron-based OCs

Fig. 1. Cycle performance of the OCs

Fig. 2.(a) N_2 adsorption/desorption isotherms of the OCs, (b) pore diameter distribution of the OCs (BJH model)

Fig. 3. SEM image of the OCs before ((a) Fe_2O_3 , (b) $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, (c) $\text{Fe}_2\text{O}_3\text{-NiO}/\text{Al}_2\text{O}_3$) and after ((e) Fe_2O_3 , (f) $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, (g) $\text{Fe}_2\text{O}_3\text{-NiO}/\text{Al}_2\text{O}_3$) reaction

Fig. 4. H_2 -TPR result of the OCs

Fig. 5. XRD patterns of the OCs before (a) and after (b) reduction reaction

Fig. 6. Thermodynamic equilibrium as a function of the CO amount fed to the system.
 $T = 900\text{ }^{\circ}\text{C}$. $P = 1\text{ bar}$

Fig. 7.Reaction mechanism of the iron-based OCs

Table 1.. $X_{max}(\%)$ and $R_{max}(\%/min)$ in each cycle of different OCs

Cycle	3			4			5		
Parameter	X_{max}	$R_{max}(\text{Re})$	$R_{max}(\text{Ox})$	X_{max}	$R_{max}(\text{Re})$	$R_{max}(\text{Ox})$	X_{max}	$R_{max}(\text{Re})$	$R_{max}(\text{Ox})$
Fe_2O_3	82.10	4.74	57.67	79.43	4.54	46.55	70.73	4.28	39.45
$\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$	90.20	19.12	71.47	91.16	18.93	72.25	92.39	18.91	71.86
$\text{Fe}_2\text{O}_3\text{-NiO}/\text{Al}_2\text{O}_3$	82.70	24.67	115.17	84.02	24.23	116.76	83.80	24.39	116.19

Table 2. BET surface area and structure properties of the OCs

OCs	S_{BET} (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
Fe ₂ O ₃	8.59	0.086	40.09
Fe ₂ O ₃ /Al ₂ O ₃	9.52	0.100	38.40
Fe ₂ O ₃ -NiO/Al ₂ O ₃	6.70	0.072	38.27

Table 3. EDX results of the OCs

Component (at% *)	Fe	O	Al	Ni
Fe ₂ O ₃	45.89	54.11	/	/
Fe ₂ O ₃ /Al ₂ O ₃	13.61	66.75	19.64	/
Fe ₂ O ₃ -NiO/Al ₂ O ₃	12.42	67.63	18.51	1.44