

Sol–Gel-Derived NiO/NiAl₂O₄ Oxygen Carriers for Chemical-Looping Combustion by Coal Char

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Chemical-looping combustion (CLC) is a very promising technology to combine the energy-utilization situation in China and CO₂ zero-emission in situ allowing for CO₂ sequestration by efficient and energy-saving ways and without nitrogen oxide (NO_x) formation. Having an oxygen carrier with sufficient reactivities in reduction and oxidation and enough recyclability and strength for long-term operation is one of the key issues of the CLC process. This paper focuses on the investigation of Ni-based oxygen carriers for CLC by coal char. First, Al(OC₃H₇)₃ and Ni(NO₃)₂ are selected as the main raw materials to prepare sol–gel-derived NiO/NiAl₂O₄ oxygen carriers. The oxygen carrier with a mass content of 60% NiO, a sintering temperature of 1300 °C, and a sintering time of 6 h performs comparatively well. Second, the reduction reaction of the NiO/NiAl₂O₄ oxygen carriers with char and the circular reduction/oxidation reactions of the NiO/NiAl₂O₄ oxygen carriers with char/air or hydrogen/air are carried out in a thermogravimetric analysis (TGA) instrument to investigate the reactivities and chemical life of the prepared NiO/NiAl₂O₄ oxygen carriers. The experimental results show that (a) when the TGA temperature is higher than 850 °C, NiO/NiAl₂O₄ starts to react with coal char rapidly, which indicates that CLC of coal char using NiO/NiAl₂O₄ as oxygen carriers is a feasible technology of energy utilization in principle; (b) NiO/NiAl₂O₄, which maintains its activity over single-cycle reduction/oxidation reactions with char/air or multiple-cycle reduction/oxidation reactions with hydrogen/air, exhibits extremely good recyclability; (c) the porous beehive structure of the NiO/NiAl₂O₄ particle is maintained, and the sintering behavior between different particles is not observed during cyclic studies. Those experimental results prove the sol–gel-derived oxygen carrier NiO/NiAl₂O₄ is capable of being used in chemical-looping combustion fueled by coal char or H₂.

1. Introduction

Chemical-looping combustion (CLC) is a new combustion technique where the CO₂ is inherently separated from nitrogen that normally makes up the main fraction of the exhaust. The oxygen carrier (usually, a metal oxide) performs the task of carrying the oxygen from the air to the fuel, and then, the direct contact of fuel and air is avoided. When fuel is being combusted in a fuel reactor (also called a reduction reactor), the metal oxide is reduced to the metallic form at the same time as fuel is oxidized to CO₂ and H₂O. The metallic particles are then circulated to an air reactor (also called an oxidation reactor) where it is reoxidized by air and a large amount of heat is liberated. The regenerated metal oxide is separated by a cyclone from the hot gases (the mixture of N₂ and O₂) and is recycled back into the fuel reactor.

CLC also exhibits its advantage in the overall thermal efficiency of processes because the irreversible exergy destruction in the two-step-reaction CLC is less than in conventional combustion of fuel.^{1,2} In addition, fuel and air go through

different reactors with no flame, which creates an opportunity to thoroughly eradicate the generation of NO_x.³

Most of studies on CLC concentrate on gaseous fuels like H₂ and methane^{4–29} because the sufficiently high reaction rate allows the process to proceed in continuous operation. CLC by gaseous fuels is suitable for those countries whose energy needs are mainly supported by gaseous fuels. However, we should

(3) Ishida, M.; Jin, H. G. A new advanced power-generation system using chemical-looping combustion. *Energy* **1994**, *19* (4), 415–422.

(4) Adanez, J.; Garcia-Labiano, F.; de Diego, L. F.; Gayan, P.; Celaya, J.; Abad, A. Nickel-copper oxygen carriers to reach zero CO and H₂ emissions in chemical-looping combustion. *Ind. Eng. Chem. Res.* **2006**, *45* (8), 2617–2625.

(5) Adanez, J.; De Diego, L. F.; Garcia-Labiano, F.; Gayan, P.; Abad, A.; Palacios, J. M. Selection of oxygen carriers for chemical-looping combustion. *Energy Fuels* **2004**, *18* (2), 371–377.

(6) Abad, A.; Mattisson, T.; Lyngfelt, A.; Ryden, M. Chemical-looping combustion in a 300 W continuously operating reactor system using a manganese-based oxygen carrier. *Fuel* **2006**, *85* (9), 1174–1185.

(7) Bannister, R. L.; Newby, R. A.; Yang, W. C. Final report on the development of a hydrogen-fueled combustion turbine cycle for power generation. *J. Eng. Gas Turbines Power, Trans. ASME* **1999**, *121* (1), 38–45.

(8) Brandvoll, O.; Bolland, O. Inherent CO₂ capture using chemical looping combustion in a natural gas fired power cycle. *J. Eng. Gas Turbines Power, Trans. ASME* **2004**, *126* (2), 316–321.

(9) Cho, P.; Mattisson, T.; Lyngfelt, A. Defluoridation conditions for a fluidized bed of iron oxide-, nickel oxide-, and manganese oxide-containing oxygen carriers for chemical-looping combustion. *Ind. Eng. Chem. Res.* **2006**, *45* (3), 968–977.

(10) Copeland, R. J.; Alptekin, G.; Cesario, M.; Gershanovich, Y. Sorbent Energy Transfer System (SETS) for CO₂ Separation with High Efficiency. *The 27th International Technical Conference on Coal Utilization and Fuel Systems*, Florida, Mar 4–7, 2002.

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(1) Anheden, M.; Svedberg, G. Exergy analysis of chemical-looping combustion systems. *Energy Convers. Manage.* **1998**, *39* (16–18), 1967–1980.

(2) Jin, H. G.; Hong, H.; Wang, B. Q.; Han, W.; Lin, R. M. A new principle of synthetic cascade utilization of chemical energy and physical energy. *Sci. China Ser. E-Eng. Mater. Sci.* **2005**, *48* (2), 163–179.

find a new mode of the CLC technique for those countries, for example, China, whose electricity demand is mainly supplied by coal. There are two routes to realize CLC by solid fuels such as coal and biomass.³⁰ Solid fuels can be used in CLC if they are first gasified by a separate gasification process and then oxidized in the fuel reactor. The disadvantages of the first route are the difficulties associated with gasification and the need for an energy intensive air separation unit. The second route is to introduce directly the solid fuels to the fuel

reactor.^{31–33} The fuel reactor would act as a gasifier, where the solid fuels react with water steam or CO₂, an oxidizer, where gaseous compounds are oxidized by the metal oxide, and a reducer, where the metal oxide is reduced to the metallic form. Here, the following technical problems must be solved:³⁴ including the interaction between fuel ash and oxygen carriers, the separation of fuel particles from the oxygen carriers, the process analysis, the potential oxygen carriers, etc. The study is mainly concerned with the oxygen carriers for CLC fueled directly by solid fuels like coal char.

There are a number of references about the metal oxides for CLC by the gaseous fuels. Ni-based,^{5,17,18,22,35–41} Cu-based,^{5,14,22,42,43} Co-based,^{18,22,36} Fe-based,^{5,18,23,38,41,44,45} and Mn-based^{5,22,45} metal oxides were initially suggested to be suitable as oxygen carriers from a thermodynamic point of view.^{4–28} These metal oxides are usually supported by the inert materials. The inert material, which could be Al₂O₃,^{5,22,35,36,43} NiAl₂O₄,^{17,18,40,46} MgO,³⁶ MgAl₂O₄,²⁸ SiO₂,^{5,14} ZrO₂,^{5,14} TiO₂,^{5,14} yttria-stabilized-

(11) Corbella, B. M.; de Diego, L.; Garcia-Labiano, F.; Adanez, J.; Palacios, J. M. Characterization and performance in a multicycle test in a fixed-bed reactor of silica-supported copper oxide as oxygen carrier for chemical-looping combustion of methane. *Energy Fuels* **2006**, *20* (1), 148–154.

(12) Corbella, B. M.; De Diego, L. F.; Garcia-Labiano, F.; Adanez, J.; Palacios, J. M. Characterization study and five-cycle tests in a fixed-bed reactor of titania-supported nickel oxide as oxygen carriers for the chemical-looping combustion of methane. *Environ. Sci. Technol.* **2005**, *39* (15), 5796–5803.

(13) Corbella, B. M.; de Diego, L. F.; Garcia-Labiano, F.; Adanez, J.; Palacios, J. M. Performance in a fixed-bed reactor of titania-supported nickel oxide as oxygen carriers for the chemical-looping combustion of methane in multicycle tests. *Ind. Eng. Chem. Res.* **2006**, *45* (1), 157–165.

(14) De Diego, L. F.; Garcia-Labiano, F.; Adanez, J.; Gayan, P.; Abad, A.; Corbella, B. M.; Palacios, J. M. Development of Cu-based oxygen carriers for chemical-looping combustion. *Fuel* **2004**, *83* (13), 1749–1757.

(15) De Diego, L. F.; Gayan, P.; Garcia-Labiano, F.; Celaya, J.; Abad, M.; Adanez, J. Impregnated CuO/Al₂O₃ oxygen carriers for chemical-looping combustion: Avoiding fluidized bed agglomeration. *Energy Fuels* **2005**, *19* (5), 1850–1856.

(16) Garcia-Labiano, F.; Adanez, J.; de Diego, L. F.; Gayan, P.; Abad, A. Effect of pressure on the behavior of copper-, iron-, and nickel-based oxygen carriers for chemical-looping combustion. *Energy Fuels* **2006**, *20* (1), 26–33.

(17) Ishida, M.; Yamamoto, M.; Ohba, T. Experimental results of chemical-looping combustion with NiO/NiAl₂O₄ particle circulation at 1200 degrees C. *Energy Convers. Manage.* **2002**, *43* (9–12), 1469–1478.

(18) Jin, H.; Okamoto, T.; Ishida, M. Development of a novel chemical-looping combustion: Synthesis of a looping material with a double metal oxide of CoO-NiO. *Energy Fuels* **1998**, *12* (6), 1272–1277.

(19) Johansson, M.; Mattisson, T.; Lyngfelt, A. Investigation of Fe₂O₃ with MgAl₂O₄ for chemical-looping combustion. *Ind. Eng. Chem. Res.* **2004**, *43* (22), 6978–6987.

(20) Lee, J. B.; Park, C. S.; Choi, S.; Song, Y. W.; Kim, Y. H.; Yang, H. S. Redox characteristics of various kinds of oxygen carriers for hydrogen fueled chemical-looping combustion. *J. Ind. Eng. Chem.* **2005**, *11* (1), 96–102.

(21) Lyngfelt, A.; Leckner, B.; Mattisson, T. A fluidized-bed combustion process with inherent CO₂ separation: application of chemical-looping combustion. *Chem. Eng. Sci.* **2001**, *56* (10), 3101–3113.

(22) Mattisson, T.; Jardnas, A.; Lyngfelt, A. Reactivity of some metal oxides supported on alumina with alternating methane and oxygen-application for chemical-looping combustion. *Energy Fuels* **2003**, *17* (3), 643–651.

(23) Mattisson, T.; Johansson, M.; Lyngfelt, A. Multicycle reduction and oxidation of different types of iron oxide particles-application to chemical-looping combustion. *Energy Fuels* **2004**, *18* (3), 628–637.

(24) Mattisson, T.; Johansson, M.; Lyngfelt, A. The use of NiO as an oxygen carrier in chemical-looping combustion. *Fuel* **2006**, *85* (5–6), 736–747.

(25) Son, S. R.; Kim, S. D. Chemical-looping combustion with NiO and Fe₂O₃ in a thermobalance and circulating fluidized bed reactor with double loops. *Ind. Eng. Chem. Res.* **2006**, *45* (8), 2689–2696.

(26) Villa, R.; Cristiani, C.; Groppi, G.; Lietti, L.; Forzatti, P.; Cornaro, U.; Rossini, S. Ni based mixed oxide materials for CH₄ oxidation under redox cycle conditions. *J. Mol. Catal. A-Chem.* **2003**, *204*, 637–646.

(27) Wolf, J.; Yan, J. Parametric study of chemical looping combustion for tri-generation of hydrogen, heat, and electrical power with CO₂ capture. *Int. J. Energy Res.* **2005**, *29* (8), 739–753.

(28) Zafar, Q.; Mattisson, T.; Gevert, B. Redox investigation of some oxides of transition-state metals Ni, Cu, Fe, and Mn supported on SiO₂ and MgAl₂O₄. *Energy Fuels* **2006**, *20* (1), 34–44.

(29) Abad, A.; Garcia-Labiano, F.; de Diego, L. F.; Gayan, P.; Adanez, J. Reduction Kinetics of Cu-, Ni-, and Fe-Based Oxygen Carriers Using Syngas (CO + H₂) for Chemical-Looping Combustion. *Energy Fuels* **2007**, *21*, 1843.

(30) Mattisson, T.; Lyngfelt, A. Applications of chemical-looping combustion with capture of CO₂. *Second Nordic Minisymposium on Carbon Dioxide Capture and Storage*, Göteborg, Oct 26, 2001.

(31) Cao, Y.; Casenas, B.; Pan, W. P. Investigation of chemical looping combustion by solid fuels. 2. Redox reaction kinetics and product characterization with coal, biomass, and solid waste as solid fuels and CuO as an oxygen carrier. *Energy Fuels* **2006**, *20* (5), 1845–1854.

(32) Gupta, P.; Velazquez-Vargas, L. G.; Li, F.; Fan, L. S. In *Chemical looping combustion of coal*; American Institute of Chemical Engineers: New York, 2005; pp 7620–7625..

(33) Gupta, P.; Velazquez-Vargas, L. G.; Thomas, T.; Fan, L. S. Chemical looping combustion of coal to produce hydrogen. In *Proceedings of the 30th International Technical Conference on Coal Utilization & Fuel Systems*, The Sheraton Sand Key Clearwater, FL, April 17–21, 2005; Sakkestad, B. A., Ed.; Coal Technology Association: The Sheraton Sand Key Clearwater, FL, 2005; p 39.

(34) Cao, Y.; Pan, W. P. Investigation of chemical looping combustion by solid fuels. 1. Process analysis. *Energy Fuels* **2006**, *20* (5), 1836–1844.

(35) Jin, H. G.; Ishida, M. Reactivity study on a novel hydrogen fueled chemical-looping combustion. *Int. J. Hydrogen Energy* **2001**, *26* (8), 889–894.

(36) Jin, H.; Okamoto, T.; Ishida, M. Development of a novel chemical-looping combustion: Synthesis of a solid looping material of NiO/NiAl₂O₄. *Ind. Eng. Chem. Res.* **1999**, *38* (1), 126–132.

(37) Ishida, M.; Jin, H. G.; Okamoto, T. A fundamental study of a new kind of medium material for chemical-looping combustion. *Energy Fuels* **1996**, *10* (4), 958–963.

(38) Ishida, M.; Jin, H. CO₂ recovery in a power plant with chemical looping combustion. *Energy Convers. Manage.* **1997**, *38*, S187–S192.

(39) Ishida, M.; Jin, H.; Okamoto, T. Kinetic behavior of solid particle in chemical-looping combustion: Suppressing carbon deposition in reduction. *Energy Fuels* **1998**, *12* (2), 223–229.

(40) Readman, J. E.; Olafsen, A.; Smith, J. B.; Blom, R. Chemical Looping Combustion Using NiO/NiAl₂O₄: Mechanisms and Kinetics of Reduction–Oxidation (Red–Ox) Reactions from In Situ Powder X-ray Diffraction and Thermogravimetry Experiments. *Energy Fuels* **2006**, *20* (4), 1382–1387.

(41) Johansson, M.; Mattisson, T.; Lyngfelt, A. Creating a Synergy Effect by Using Mixed Oxides of Iron and Nickel Oxides in the Combustion of Methane in a Chemical-Looping Combustion Reactor. *Energy Fuels* **2006**, *20* (6), 2399–2407.

(42) Corbella, B. M.; De Diego, L.; Garcia, F.; Adanez, J.; Palacios, J. M. The performance in a fixed bed reactor of copper-based oxides on titania as oxygen carriers for chemical looping combustion of methane. *Energy Fuels* **2005**, *19* (2), 433–441.

(43) Adanez, J.; Gayan, P.; Celaya, J.; de Diego, L. F.; Garcia-Labiano, F.; Abad, A. Chemical Looping Combustion in a 10 kWth Prototype Using a CuO/Al₂O₃ Oxygen Carrier: Effect of Operating Conditions on Methane Combustion. *Ind. Eng. Chem. Res.* **2006**, *45* (17), 6075–6080.

(44) Ishida, M.; Jin, H. G.; Okamoto, T. Kinetic behavior of solid particle in chemical-looping combustion: Suppressing carbon deposition in reduction. *Energy Fuels* **1998**, *12* (2), 223–229.

(45) Cho, P.; Mattisson, T.; Lyngfelt, A. Comparison of iron-, nickel-, copper- and manganese-based oxygen carriers for chemical-looping combustion. *Fuel* **2004**, *83* (9), 1215–1225.

(46) Jin, H.; Ishida, M. Reactivity study on a novel hydrogen fueled chemical-looping combustion. *Int. J. Hydrogen Energy* **2001**, *26* (8), 889–894.

zirconium (YSZ),^{36,37,44,46} kaolin, sepiolite,⁵ bentonite,⁴⁷ and hexaaluminate, imparts the following characteristics to the oxygen carriers: reactivity, crushing strength, sintering temperature, and durability. The preparation method of the oxygen carriers, which could be mechanical mixing, extrusion, impregnation, spray-drying, freeze-granulation, and sol-gel, is another field of research. It was found that different inert materials, different proportions of mixture, different preparation methods, and different preparation processes affect the physicochemical performance of oxygen carriers.^{37,48}

The oxygen carriers for CLC by gaseous fuels could provide a starting point for the identification of oxygen carriers for CLC by solid fuels. However, as far as CLC by solid fuels is considered, the reduction reactivity between the solid fuels and the solid oxygen carriers is the primary technical concern. Fan and co-workers^{32,33} investigated the reduction reactivity between coal and Fe₂O₃, in which a good reaction above 1023 K leading to high conversions to Fe is observed. Lyngfelt and co-workers⁴⁹ demonstrated the feasibility of using petroleum coke in CLC supported by Fe₂O₃/MgAl₂O₄ oxygen carriers. Pan and co-workers^{31,34} established the theoretical frame of oxygen transfer capability, reaction enthalpy, a chemical equilibrium, and kinetics and then suggested CuO-Cu-, NiO-Ni-, and CoO-Co-based oxygen carriers for use in chemical-looping combustion by solid fuels. Furthermore, Pan et al.³¹ evaluated the reduction reaction of CuO with solid fuels such as coal, biomass, and solid waste. However, Fe-based oxygen carriers have disadvantages in their larger endothermic enthalpy and lower reactivity; Cu-based oxygen carriers have the disadvantage of a tendency to agglomerate at lower operation temperatures (<900 °C).

Ishida and co-workers¹⁷ produced NiO/NiAl₂O₄ oxygen carriers by a dissolution method. The NiO/NiAl₂O₄ particles for CLC fueled by hydrogen perform with good circulation properties, high reactivity, and high mechanical strength at 1200 °C. The experimental tests on the direct reduction reaction of NiO/NiAl₂O₄ oxygen carriers by the selected solid fuels (coal char) are also conducted in the paper. Different from the NiO/NiAl₂O₄ particles prepared by the dissolution method, it is prepared by the sol-gel method. Thermogravimetric analysis (TGA) in a microreactor is used to evaluate the reduction reaction between NiO/NiAl₂O₄ and coal char through analyzing the weight of the mixture as a function of time and temperature, and an X-ray diffractometer (XRD), a scanning electron microscope (SEM), and a N₂ adsorption-desorption (BET) methods are utilized to characterize the solid residues.

2. Experimental Details

2.1. Preparation of Oxygen Carriers by the Sol-Gel Method.

The sol-gel process is a method for the production of inorganic materials at ambient temperature, and it provides a convenient method for incorporation, immobilization, entrapment, and encapsulation of a large variety of materials including organics, inor-

(47) Siriwardane, R.; Poston, J.; Chaudhari, K.; Zinn, A.; Simonyi, T.; Robinson, C. Chemical-Looping Combustion of Simulated Synthesis Gas Using Nickel Oxide Oxygen Carrier Supported on Bentonite. *Energy Fuels* **2007**, *21* (3), 1582–1591.

(48) Adanez, J.; de Diego, L. F.; Garcia-Labiano, F.; Gayan, P.; Abad, A.; Palacios, J. M. Selection of oxygen carriers for chemical-looping combustion. *Energy Fuels* **2004**, *18* (2), 371–377.

(49) Leion, H.; Mattisson, T.; Lyngfelt, A. The use of petroleum coke as fuel in chemical-looping combustion. *Fuel* **2007**, *86* (12–13), 1947–1958.

Table 1. Classification of the NiO/NiAl₂O₄ Oxygen Carriers

oxygen carrier type	mass content of NiO (%)	sintering temperature (°C)	sintering time (h)
N6AN1306	60	1300	6
N6AN1310	60	1300	10
N6AN1406	60	1400	6
N4AN1306	40	1300	6
N4AN1310	40	1300	10
N4AN1406	40	1400	6

ganics, biomolecules, microorganisms, tissue, and indicators.^{50,51} The sol-gel process, as its name implies, involves the formation of a colloidal suspension (sol) and gelation of the sol to form a wet gel (a globally connected solid matrix), which after drying forms a “dry gel” state (xerogel).

The following steps summarize the preparation of NiO/NiAl₂O₄ oxygen carriers by the sol-gel process: (1) Preparation of boehmite sol. A kind of low molecular weight trialkoxide, aluminum isopropoxide (Al(OC₃H₇)₃), is selected as a gel precursor to prepare boehmite (AlOOH) sol. A solvent, nitric acid (HNO₃), is used as catalyst for homogenization because alkoxysilanes are not miscible with water. The exact Yoldas process was used to prepare the high concentration boehmite sol. It includes hydrolysis (85 °C, 1.5 h) and condensation (90 °C, 0.5 h) of 45.386 g Al(OC₃H₇)₃ (chemical pure) in 400 mL distilled water and peptization (90 °C, 12 h) with HNO₃ of 1 mol/L in the amount that gave the H⁺/Al³⁺ ratio of 0.07. The resulting γ -AlOOH sol is concentrated by letting it stand for 0.5 h in air to evaporate the remaining alcohol group. (2) Preparation of γ -AlOOH wet gel with the deconcentrated nickel nitrate. The nickel nitrate solution (Ni(NO₃)₂·6H₂O, analytical pure; the concentration depends on the required NiO amount of coating, varied from mass concentration 40–60%) is dropped into the γ -AlOOH sol at 90 °C in the condition of fully stirring. The resulting green wet gel is stirred for 0.5 h in order to reach a good deconcentration condition. (3) Preparation of NiO/NiAl₂O₄ particles. The wet gel is dried for 36 h at 85 °C, 5 h at 100 °C, 5 h at 150 °C, and 5 h at 200 °C, in a step by step manner. The stepwise drying is to avoid the breakage of the derived light-grayish-green xerogel. The resulting low-intensity Ni(OH)₂/Al₂O₃ pieces are then calcined in a electric muffle furnace for 3 h at 450 °C and for 3 h at 650 °C, step by step. The resultant faint-yellow NiO/Al₂O₃ pieces are of lower intensity than the above Ni(OH)₂/Al₂O₃ pieces. And then, the NiO/Al₂O₃ pieces are calcined in the electric muffle furnace for 6 or 10 h at 1300 or 1400 °C. The resultant yellowish green NiO/NiAl₂O₄ pieces are high intensity and are then ground in a miller and sieved through the screen sizing method. To this point, derived sol-gel NiO/NiAl₂O₄ particles with sizes of 125–180 μ m are obtained.

Depending on the different contents of NiO, the different sintering temperatures, and the different sintering hours, six types of NiO/NiAl₂O₄ oxygen carriers are produced, which are summarized in Table 1.

2.2. Physicochemical Characterization of NiO/NiAl₂O₄ Oxygen Carriers. The chemical reactivity of the oxygen carriers with solid fuels (char) is carried out in a Thermo500 TGA from Thermo Cahn cooperation. Coal char is prepared in the electric muffle furnace through calcining the Shenfu coal, a Chinese coal, with sizes of under 150 μ m at 900 °C for 7 min. The proximate and elemental analysis of Shenfu coal and Shenfu coal char are summarized in Table 2. The size fraction of coal char is in the range of 50–150 μ m. The mass ratios of char and the different NiO/NiAl₂O₄ are determined according to the stoichiometric ratio of the fixed carbon in the char and the active oxygen in the different oxygen carriers, which is listed in Table 3. The NiO/NiAl₂O₄ oxygen carrier is sieved into particles with a size fraction of

(50) El-Nahhal, I. M.; El-Ashgar, N. M. A review on polysiloxane-immobilized ligand systems: Synthesis, characterization and applications. *J. Organomet. Chem.* **2007**, *692*, 2861–2886.

(51) Wang, Z. M.; Lin, Y. S. Sol-Gel Synthesis of Pure and Copper Oxide Coated Mesoporous. *J. Catal.* **1998**, *174*, 43–51.

Table 2. Approximate and Elemental Analysis of the Shenfu Coal and Coal Char

sample	approximate analysis (wt %, as received basis)				elemental analysis (wt %, dry basis)				
	moisture	volatile matter	ash	carbon	C	H	N	S _t	O
Shenfu coal	10.19	31.62	5.84	52.35	80.53	4.80	0.89	0.40	13.38
Shenfu coal char	4.578	7.588	10.754	77.080	79.130	0.794	0.841	0.285	18.950

Table 3. Mass Ratio of Char and Oxygen Carrier NiO/NiAl₂O₄

oxygen carrier type	char:oxygen carrier (mass ratio)
N6AN1306	3:50
N6AN1310	3:50
N6AN1406	3:50
N4AN1306	2:50
N4AN1310	2:50
N4AN1406	2:50

125~180 μm. About 10 mg of coal char and NiO/NiAl₂O₄ particles are ground together using a mortar and pestle to provide for high dispersion into each other. The reaction temperature is 900 °C. The reduction reaction between char and NiO/NiAl₂O₄ is characterized by the weight of the mixture as a function of time in an inert environment of nitrogen. The single reduction/oxidation cycle of NiO/NiAl₂O₄ particles with char/air is also carried out in the TGA setup. When the weight of NiO/NiAl₂O₄ and char particles becomes nearly constant at 900 °C, the reaction chamber is swept by feeding inert gas N₂ with flux of 100 mL/min, and then, air with a flux of 100 mL/min is introduced to let the metal Ni be oxidized at 1000 °C. The weight of particles is recorded continuously to evaluate the chemical reactivity of the NiO/NiAl₂O₄ oxygen carriers with char.

The recyclability of NiO/NiAl₂O₄ particles is studied by the cyclic reduction/oxidation reaction of NiO/NiAl₂O₄ with hydrogen in the TGA setup. The reducing gas mixture with a flux of 100 mL/min is 50% hydrogen in nitrogen, and the oxidizing condition is simulated using air with a flux of 100 mL/min. When the weight of the particles is become constant in the existence of H₂ at 900 °C, it is considered that the reduction reaction is finished. After the reaction chamber is swept by feeding inert gas with flux of 100 mL/min for several minutes, air is fed to allow the oxidation reaction to be realized at 900 °C. This cycle of reduction and oxidation reaction is repeated five times.

The final samples are analyzed by an X'Pert PRO X-ray diffractometer (XRD) using Cu Kα radiation from the PANALAB Company of Netherlands. A ceram X-ray tube is equipped with a maximum power of 2.2 kW, the maximum voltage of 60 kV, and the maximum current of 55 mA. The samples are scanned from 10–90°. The surface of the particles is examined by a Sirion200 emission scanning electron microscope (SEM) from the FEI Company. The pore structure of oxygen carriers is measured by specific surface area and pore size analyzer (ASAP2000) of the Mike Equipment Company (USA) using the N₂ adsorption-desorption method.

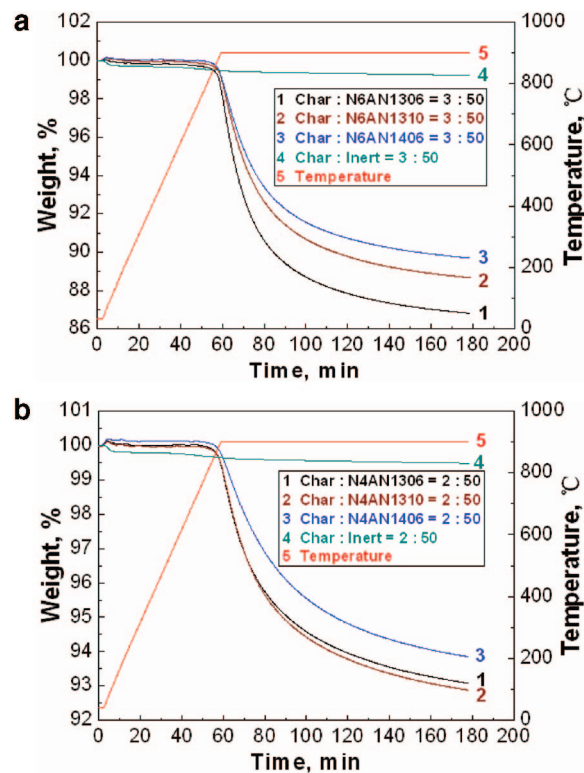
3. Results and Discussion

3.1. Chemical Reactivity of NiO/NiAl₂O₄ Oxygen Carriers with Char. The reduction reaction of NiO/NiAl₂O₄ oxygen carriers with coal char is carried out in the TGA setup. Figure 1a and b shows the results of N6AN and N4AN oxygen carriers by TGA, respectively. In the two graphs, curve 4 represents the results of a blank experiment or contrastive experiment, that is, the reactive oxygen carriers are replaced by the insert material SiO₂ with the equal amount of oxygen carriers; curve 5 is the temperature as a function of time in the TGA. The blank experiment allows our results to be compared with the results of NiO/NiAl₂O₄ + char and describes the weight loss of char due to the evaporation of the remnant water and volatile substance. Curves 1–3 show the weight loss of the mixture

that is composed of char and the different types of NiO/NiAl₂O₄ oxygen carriers.

As shown in Figure 1, the weight of mixture sample begins to decrease rapidly around 850 °C, and the falling rates are far greater than curve 4 of the blank experiment, which shows that the chemical reaction between NiO/NiAl₂O₄ oxygen carriers and coal char begins to carry through around 850 °C, that is, solid fuels such as coal char can be reacted with oxygen carriers such as NiO/NiAl₂O₄ at high temperatures (>850 °C).

As shown in Figure 1, the mixture sample of the N6AN1306 oxygen carrier and char loses more weight than that of N6AN1310 + char and N6AN1406 + char (in that order), which shows that the chemical reactivity of the N6AN1306 oxygen carrier with char is higher than that of N6AN1310 and N6AN1406 (in that order). Likewise, the chemical reactivity of the N4AN1306 and N4AN1310 oxygen carriers is higher than that of N4AN1406, as shown in Figure 1b. Those results indicate that the lower sintering temperature and the shorter sintering time during the preparation of NiO/NiAl₂O₄ oxygen carriers by the sol-gel method help improve the chemical reactivity of the NiO/NiAl₂O₄ oxygen carriers. However, the results in the TGA setup show the N4AN1310 oxygen carrier is more reactive than the N4AN1306 oxygen carrier in a way, which seems to conflict with the above general conclusion on the sintering temperature and time. In fact, the TGA results are associated with the mixability of the sample particles. The displacement between curve 1 and 2 in Figure 1b may be a result of the uneven mixing of the N4AN1310 particles and char particles. On the other hand, the component NiAl₂O₄ in

**Figure 1.** TGA results in the reduction reaction between (a) the N6AN oxygen carriers and char, and (b) the N4AN oxygen carriers and char.

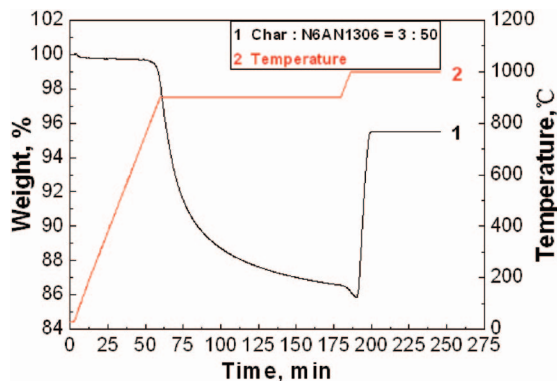


Figure 2. TGA results in the single-cycle reduction/oxidation reaction between the N6AN1306 oxygen carrier and char/air.

the N4AN oxygen carriers may be the thermodynamics-unstable phase Ni–Al–O, and the phase Ni–Al–O may consume parts of active oxygen of NiO and then contribute partly to the displacement between curve 1 and 2 in Figure 1b.

If the following reaction between NiO/NiAl₂O₄ oxygen carriers and char is thoroughly completed,



the mass of the residual mixture (it should be Ni and NiAl₂O₄ in theory) is 83.3% of the initial mass for the N6AN oxygen carriers and 88.7% of the initial mass for the N4AN oxygen carriers. The less the mass of the residual mixture, the higher chemical reactivity the associated NiO/NiAl₂O₄ oxygen carriers exhibit. When the N6AN1306 oxygen carrier reacts with char in the TGA setup, the mass of the residual mixture after 180 min reaches 86.5% of the initial mass, as shown in Figure 1a; when the mixture of the N4AN1306 and char particles is considered, the final mass after 180 min is about 92.5% of the initial mass, which can be observed in Figure 1b. These results indicate the reduction reaction between char and the N6AN1306 or N4AN1306 oxygen carriers is nearly completed, and the N6AN1306 oxygen carrier has the highest chemical reactivity among the six types of NiO/NiAl₂O₄ oxygen carriers. At the same time, the N6AN oxygen carriers possess higher transport capacity for oxygen over the N4AN oxygen carriers, which indicates that less mass of oxygen carriers in the two-fluidized bed reactor²¹ for the chemical-looping combustion is required. Summing up, the sol–gel-derived N6AN1306 oxygen carrier has good chemical reactivity and enough transport capacity for oxygen, and it is selected as the potential oxygen carrier for chemical-looping combustion by coal char.

As for the real CLC system, first, NiO/NiAl₂O₄ oxygen carriers react with char, and the gaseous mixture of CO₂, H₂O, and the reduced Ni is produced. And then, the oxidation reaction between Ni and O₂ from air is carried out, and the metal oxide NiO is reproduced. The cycling reduction–oxidation reaction of oxygen carriers with fuel/air proceeds in a two-stage, interconnected fluidized bed reactor to realize the chemical-looping combustion. However, the cyclic feed of char particles is impossible in the TGA setup. So, we only tested the single-cycle reduction–oxidation reaction of the N6AN1306 oxygen carrier with char/air in the TGA setup, which is shown in Figure 2. Here, curve 2 is the temperature as a function of time; curve 1 represents the weight loss of the mixture. When the mass of the mixture of N6AN1306 and char particles decreases to 86.5% of the initial mass, it is considered that the reduction reaction between NiO and char is nearly completed, and air enters the TGA microreactor. It is observed from curve 2 of Figure 2 that the mass of the mixture decreases rapidly once air enters. It is

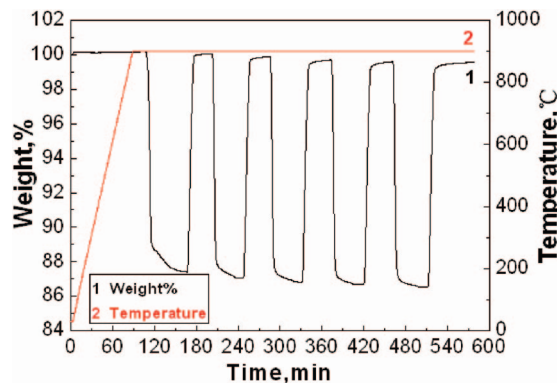


Figure 3. TGA results in the multiple-cycle reduction/oxidation reaction between the N6AN1306 oxygen carrier and hydrogen/air.

because the residual char reacts quickly with O₂ from air, that is, C + O₂ → CO₂. And then, the mass of the particles increases rapidly because the reduced Ni reacts with O₂ from air. Lastly, the mass of the particles becomes constant.

Nevertheless, it is worth noting that the reduction rate of coal char with NiO/NiAl₂O₄ oxygen carriers is slow in the temperature range of 850–900 °C, especially compared with the high oxidation rate of the reduced Ni with O₂. Two ill-matched reaction rates will greatly restrict the realization of chemical-looping combustion of coal. So, the effect of the reaction environment, for example, reaction temperature and pressure and sufficient mixing between the oxygen carrier particles and char particles, on the reduction rate should be further considered.

3.2. Cyclic Reduction/Oxidation Reaction of the N6AN1306 Oxygen Carrier with Hydrogen/Air.

It is very difficult to separate the ashes from the residual particles and the cyclic feed of coal char particles is intractable in a TGA setup at the present time. The ash separation and the cyclic feed of coal char particles are necessary for the multiple-cycle reduction/oxidation reaction between the N6AN1306 oxygen carriers and char/air in a TGA setup. Although the multiple-cycle reduction/oxidation reaction between the N6AN1306 oxygen carriers and hydrogen/air may be not suitable to evaluate the multiple reduction/oxidation cyclic reactivity of the oxygen carrier, the cyclic reduction/oxidation reaction of oxygen carriers with hydrogen/air is capable of evaluating the physical performance of oxygen carriers after several reduction/oxidation cycles and will provide some useful information for evaluating the recyclability of oxygen carriers with coal char.³³ The recyclability of the N6AN1306 oxygen carrier with hydrogen/air is tested through the cyclic feeding of hydrogen and air in the TGA setup. Figure 3 shows the TGA results. The cycle of reduction and oxidation reaction is repeated five times. Curve 2 in Figure 3 represents the mass change of the oxygen carriers during the cyclic reduction/oxidation studies. The experimental results show that the N6AN1306 oxygen carrier maintains its reactivity over multiple reduction/oxidation cycles. The weight loss history of the N6AN1306 oxygen carrier in the five-cycle reduction/oxidation reactions with hydrogen/air is listed in Table 4. As the circulation proceeds, the reduction degree of the oxygen carriers is gradually intensified; however, the rate of the reduction intensification decreases gradually. The reduction intensification may be ascribed to the formation of the bigger inner pore of particles by the thermal shock and chemical reaction. On the other hand, the oxidation degree of the oxygen carriers is gradually degraded along with the process of circulation. The oxidation degradation may be ascribed to the devitalization of parts of the metal Ni that is reduced by NiO during the circulation. Similarly, the rate of the oxidation

Table 4. Weight loss history of the N6AN1306 oxygen carriers in the five-cycle reduction/oxidation reactions with hydrogen/air

cycle number	1	2	3	4	5
mass ratio after one oxidation reaction (%)	100.07	99.88	99.71	99.61	99.58
mass ratio after one reduction reaction (%)	87.40	87.07	86.82	86.68	86.54
the difference of mass ratio after one cyclic reaction (%)	12.67	12.81	12.89	12.93	13.04

degradation also decreases gradually. However, the rate of the oxidation degradation is lower than the rate of the reduction intensification. So, the reduction–oxidation reactivity of the oxygen carriers increases by degrees on the whole.

3.3. Characterization of the Fresh and Used Oxygen Carriers. In order to determine the chemical transformations that occurred in the particles, all the samples are characterized prior to and following reactivity testing using the X-ray diffractometer (XRD). The XRD pattern of the fresh N6AN1306 oxygen carriers is shown in Figure 4a. There are only two phases, NiO and NiAl₂O₄, in the oxygen carriers and no Al₂O₃ phase, which proves that Al₂O₃ and NiO have a thorough reaction that generated NiAl₂O₄. NiAl₂O₄ is an inert carrier and has no transport capacity for oxygen in the reactions.

The XRD pattern of the char + N6AN1306 mixture after undergoing the reduction reaction is shown in Figure 4b. There are five phases: the unreacted metal oxide NiO, the reduced Ni, NiAl₂O₄, Al₂O₃, and Ni₂SiO₄. The Al₂O₃ phase should be mostly arising from char ashes; of course, a small part of it also results from the reduction of the carrier NiAl₂O₄ with char or the gasifying products of NiAl₂O₄. The Ni₂SiO₄ phase is attributed to the reaction of NiO and SiO₂ from char ashes. And a small part of NiAl₂O₄ is also ascribed to the reduction of NiO and Al₂O₃ from char ashes; of course, most of the NiAl₂O₄ is still the inert material of oxygen carriers. The XRD characterization of the solid residue samples after the single-cycle reduction/oxidation/reduction, which is shown in Figure 4c, gives clear evidence that the reduced Ni is completely oxidized

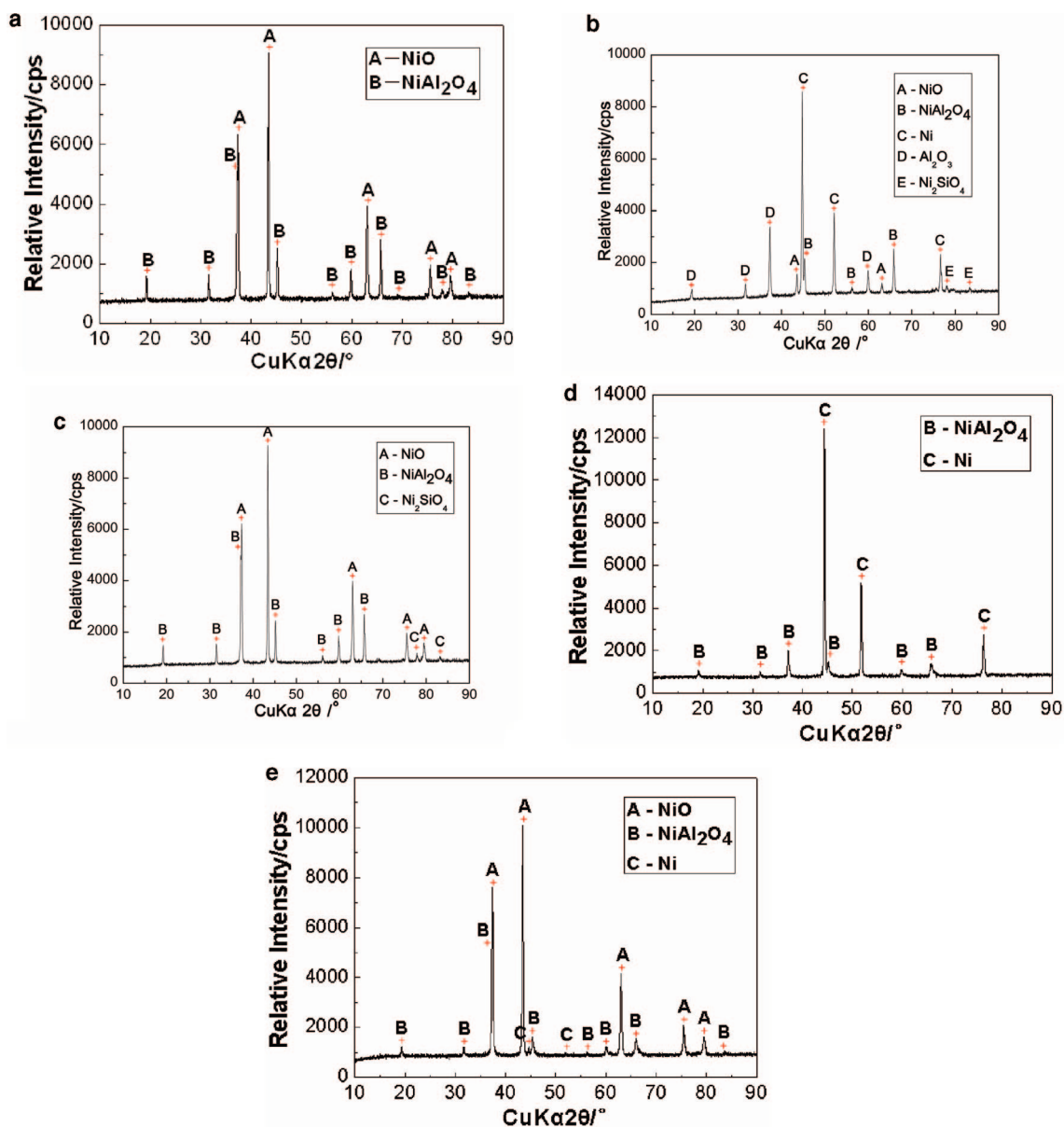


Figure 4. XRD characterization of the fresh and used NiO/NiAl₂O₄ oxygen carriers. (a) Fresh N6AN1306. (b) N6AN1306 after the reduction reaction with char. (c) N6AN1306 after the single-cycle reduction/oxidation reaction with char/air. (d) N6AN1306 after the fifth reduction reaction with H₂/air. (e) N6AN1306 after the fifth oxidation reaction with H₂/air.

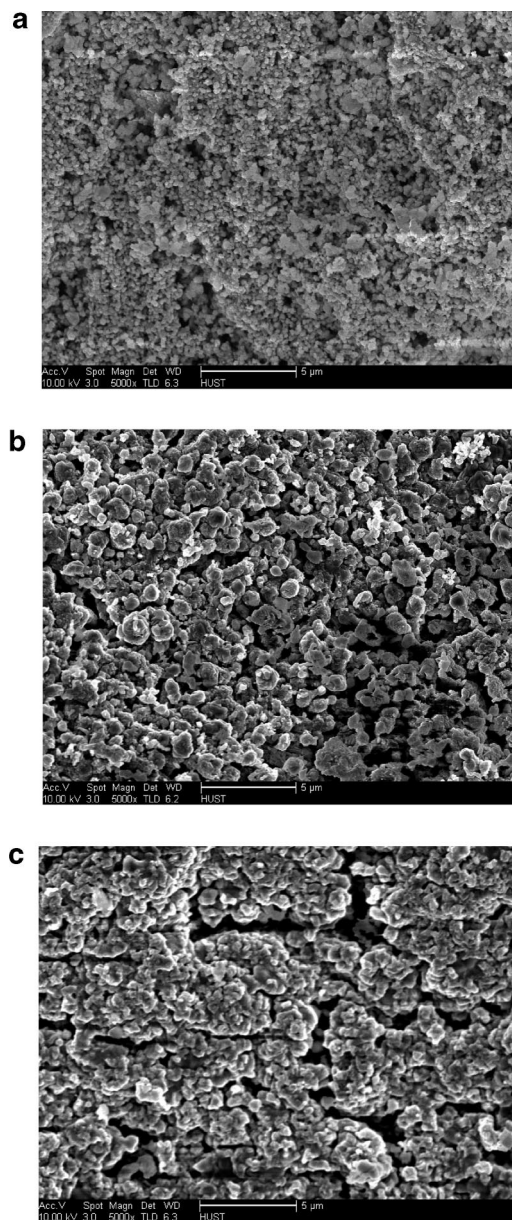


Figure 5. SEM images for the fresh and used NiO/NiAl₂O₄ oxygen carriers. (a) Fresh N6AN1306. (b) N6AN1306 after the single-cycle reduction/oxidation reaction with char/air. (c) N6AN1306 after the multiple-cycle reduction/oxidation reaction with H₂/air.

by O₂ from the air, and the lattice oxygen of the oxygen carriers is fully restored. It is worth noting that there still exists an Ni₂SiO₄ phase, which indicates that the char ashes have remarkable effect on the oxidation/reduction between coal char and oxygen carriers.

The XRD characterization of NiO/NiAl₂O₄ oxygen carriers after the five cyclic reactions with H₂/air is shown in Figure 4d and e. After the fifth reduction reaction, the solid residue sample

is composed of the metal Ni and the insert material NiAl₂O₄, which indicates that the reactive NiO is completely reduced by H₂. After the fifth oxidation reaction, the solid residue sample is composed of the devitalized metal Ni, the metal oxide NiO, and the insert material NiAl₂O₄. The XRD characterization of the two residue samples after the cyclic reduction/oxidation reaction agrees with the TGA results.

Also, the shape and morphology of both the fresh and reacted oxygen carrier particles are studied using the scanning electron microscope (SEM). Figure 5a shows the surface morphology of the fresh N6AN1306 sample. It is observed that the spherical particles are composed of individual grains, and the diameter of the grains in the surface is less than 1 μm. Hence, the pore size is very small, too. The porous structure results in the large specific area of the oxygen carrier particles, which will help increase the chemical reactivity of the oxygen carriers.

After the single-cycle experiment of the N6AN1306 oxygen carriers with char/air, its surface is changed, as shown in Figure 5b. It is found that the diameter of the individual grains reaches about 1–2 μm, and the pore size is larger than that of the fresh sample. The sintering behavior between different particles is not observed, and the porous beehive structure of particle is maintained after the reduction/oxidation reactions.

After the cyclic reduction/oxidation reaction of the N6AN1306 oxygen carrier with hydrogen/air, the N6AN1306 sample shows the clear enlargement of individual grains about 2–3 μm in diameter and of individual pores about 1–6 μm in length and about 1 μm in width, as shown in Figure 5c. Although the sintering among individual grains in the same particle surface results in the slight decrease of the specific area of the particles, the porous oxygen carrier particles still maintain good reactivity.

The above experimental results prove that the sol–gel-derived NiO/NiAl₂O₄ particles have good stability after the single- or multiple-cycle reduction/oxidation reaction with solid/gaseous fuels, which is very important for long-term operation in chemical-looping combustion by solid/gaseous fuels.

The N₂ physisorption by the Brunauer–Emmett–Teller (BET) method in a micromeritics ASP2000 is used to measure the pore structure of the fresh and reacted oxygen carriers. The BET data is listed in Table 5. The fresh N6AN1306 and N4AN1306 sample particles have the largest specific surface area (m²/g), the largest volume inside the pore (cm³/g), and the largest average pore size (Å) among the N6AN and N4AN oxygen carriers, respectively. This is because the longer sintering time and the higher sintering temperature result in larger individual grains on the surface of the oxygen carriers particles and the larger pore in the inside of the particles. From the viewpoint of the pore structure, BET data can also explain why the N6AN1306 and N4AN1306 oxygen carriers demonstrate the highest reactivity among the same series of oxygen carriers during the reduction reaction, as shown in Figure 1a and b.

After the single-cycle reduction/oxidation reaction, the specific surface area, pore volume, and size of the N6AN1306 particles increase slightly, and the pore structure is still

Table 5. BET Data for the Fresh and Used NiO/NiAl₂O₄ Oxygen Carriers

oxygen carrier	specific surface area (m ² /g)	volume inside the pore (cm ³ /g)	average pore size (Å)
fresh N6AN1306	2.360	0.025	112.408
fresh N6AN1310	1.940	0.017	99.324
fresh N6AN1406	0.729	0.008	86.123
fresh N4AN1306	3.092	0.034	229.047
fresh N4AN1310	2.408	0.028	121.403
fresh N4AN1406	0.679	0.006	66.407
reacted N6AN1306 after single-cycle reaction with char/air	2.457	0.026	118.915
reacted N6AN1306 after multiple-cycle reaction with hydrogen/air	1.856	0.021	137.424

maintained, although the residual ash from char may clog the pore of the reacted particles. On the other hand, after the five cyclic reduction/oxidation reactions with H₂/air, the specific surface area and pore volume of the N6AN1306 particles slightly decrease and the pore size slightly increases. The change should be ascribed to the internal sintering of the grains. However, the pore structure is still maintained, which supports its high recyclability and stability in the chemical-looping combustion by H₂.

4. Conclusions

Chemical-looping combustion (CLC) is a very promising technology to combine fuel combustion and pure CO₂ production. Little information is available where solid fuels such as coal are used as the energy resource in a CLC process. One of the key issues of the technology is the development of oxygen carriers with sufficient reactivity in reduction and oxidation and enough recyclability and stability. Several types of sol-gel-derived NiO/NiAl₂O₄ oxygen carriers are prepared with different NiO contents, sintering temperatures, and sintering times and, then, are utilized to carry out the reduction reaction with char of Shenhu coal, the single-cycle reduction/oxidation reaction with char/air, and the multiple-cycle reduction/oxidation reaction with hydrogen/air in a TGA setup. XRD, SEM, and BET are used to characterize these fresh and used NiO/NiAl₂O₄ samples. The experimental results shows that (1) when the TGA temperature is higher than 850 °C, NiO/NiAl₂O₄ starts to react with coal char rapidly, in which the N6AN1306 oxygen carrier with a mass content of 60% NiO, a sintering temperature of 1300 °C, and a sintering time of 6 h, demonstrating the comparatively good reduction reactivity; (2) the N6AN1306 oxygen carriers exhibit good recyclability with char/air; (3) the N6AN1306 oxygen carriers demonstrate extremely good recyclability of the reduction/oxidation reaction with hydrogen/air (It is worth noting that the reduction/oxidation reactivity of the oxygen carriers with hydrogen/air increases by degrees); (4) the sintering behavior between different particles is not observed,

and the porous beehive structure of the particle is maintained after the cyclic reduction/oxidation reaction with char/air or hydrogen/air, which proves that N6AN1306 oxygen carrier has good stability for long-term operation. These experimental results show promise in the development of the chemical-looping combustion of coal, based on NiO/NiAl₂O₄ oxygen carriers.

The TGA setup provides a well-conditioned reaction environment and is capable of evaluating the chemical and physical characteristics of oxygen carriers to a certain extent. TGA results will benefit the choice of oxygen carriers with different oxides, different inner materials, different contents of mixture, different preparation methods, and different preparation processes. Furthermore, TGA results also provide some useful information about the reduction rate, the oxidation rate, the reaction temperature, etc. Those obtained parameters will be very useful as for the design and operation of the reactors of CLC, for example, a two-stage, interconnected fluidized bed reactor. However, the reaction environment in a TGA setup is much different from that in a real reactor (generally, a fluidized bed reactor) of a CLC system. In a fluidized bed reactor, the high dispersion between solid fuels and oxygen carriers, which happens in a TGA setup, may be difficult to realize. The optimal preparation method of oxygen carriers may be one of solutions for this issue. If the density of oxygen carriers is close to the density of solid fuels, the high dispersion between the two kinds of solid particles in a fluidized bed is possible. In the next stage of research, the multiple-cycle reduction/oxidation reaction of the NiO/NiAl₂O₄ oxygen carriers with char/air in a fluidized bed reactor will be carried out.

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