

NiO/NiAl₂O₄ oxygen carriers prepared by sol-gel for chemical-looping combustion fueled by gas

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Abstract: Chemical-looping combustion with inherent CO₂ enrichment depends on the high-powered oxygen carriers. Ni(NO₃)₂ and Al(OC₃H₇)₃ are selected as the main raw materials to prepare sol-gel-derived NiO/NiAl₂O₄, by matching the appropriate experimental parameters. 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 good physicochemical properties. The circular reduction–oxidation reaction between NiO/NiAl₂O₄ and methane/air has been investigated with the help of a thermogravimetric analyzer (TGA). X-ray diffraction (XRD), scanning electron microscope (SEM), and the N₂ adsorption–desorption (BET) methods were utilized to characterize the physicochemical properties of the fresh and used oxygen carriers. The experimental results show that the sol-gel-derived NiO/NiAl₂O₄ oxygen carriers demonstrate an extremely good recycling ability of reduction–oxidation reaction. The reduction of NiO occurs in the presence of CH₄, and the reduced Ni is oxidized to NiO in air. As the circulation proceeds, the reduction degree is gradually intensified and the oxidation degree is gradually alleviated. The rates of the reduction intensification and the oxidation alleviation decrease gradually, and then the reduction–oxidation reactivity of the oxygen carriers increases by degrees. The sintering behavior between different particles is not observed, and the porous beehive structure of the particle is maintained after several circle reduction–oxidation reactions. These experimental results prove that the sol-gel-derived oxygen carrier NiO/NiAl₂O₄ is capable of being equipped by chemical-looping combustion fueled by CH₄.

Key Words: chemical-looping combustion; oxygen carriers; sol-gel; NiO/NiAl₂O₄; CO₂ enrichment

In the conventional combustion processes of fossil fuel, a fraction of CO₂ is only 10–14% in the exhaust because of the dilution of N₂. The energy consumption for CO₂ separation is very high. Combining novel energy conversion principle with CO₂ enrichment is no doubt a revolutionary technique to solve the utilization of fossil fuel as well as to protect the environment. Chemical-looping combustion (CLC), which is based on the looping of oxygen carriers, performs naturally low energy consumption for CO₂ enrichment, high efficiency of energy conversion, as well as a low emission of regular pollutants (NO_x, SO_x, etc.). These advantages of CLC technology motivate its development.

Chemical-looping combustion, based on the cascade utilization of chemical energy^[1], utilizes lattice oxygen from oxygen carriers, which are usually metal oxides, to complete the combustion of fuel. It consists of two cascade reactors: an air reactor (also called oxidation reactor) and a fuel reactor (also called reduction reactor). When the metal oxide reacts with fuel in the fuel reactor, the metal oxide is reduced to the

metallic form and at the same time the fuel is oxidized to CO₂ and H₂O. This means that pure CO₂ can be obtained through condensing H₂O, and subsequently, CO₂ enrichment can be realized with low energy consumption. The metallic particles are then circulated to the air reactor where they are reoxidized by air and a large amount of heat is liberated. The regenerated metal oxide is recycled back into the fuel reactor.

The oxygen carrier with high performance is one of the key issues of successful CLC systems. At present, particular attention is paid to the oxygen carrier for CLC by gaseous fuels. The popular metallic oxygen carriers include Fe-, Cu-, Ni-, Mn-, and Co-based metal oxides, and double metal oxides^[2]. These metal oxides are usually supported by inert materials through some preparation processes. These inert materials may be Al₂O₃, SiO₂, MgO, TiO₂, ZrO₂, YSZ, hexaaluminate, sepiolite, and so on^[2]. The available preparation methods include mechanical mixing, extrusion, impregnation, spray-drying, freeze-granulation, sol-gel, and

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so on^[2]. It has been found that inert materials, proportions of a mixture, preparation methods, and preparation processes affect the physicochemical performance of oxygen carriers^[3,4].

The following oxygen carriers perform good chemical reactivity^[2]: NiO/NiAl₂O₄ prepared by dissolution or the spray-drying method, NiO/YSZ prepared by dissolution or the sol-gel method, Fe₂O₃/Al₂O₃ prepared by the mechanical mixing method, Cu-based oxygen carrier prepared by mechanical mixing or the impregnation method, CoO/YSZ prepared by the dissolution method, Mn₃O₄/ZrO₂ prepared by mechanical mixing, and CoO-NiO/YSZ prepared by the dissolution method. However, Cu-based oxygen carriers are restrained on account of their poor temperature-bearing capacity (≈800°C); NiO/YSZ and CoO/YSZ oxygen carriers have low crushing strength and subsequently fragmentation occurs on the surface during the circulation processes. Comparatively speaking, NiO/NiAl₂O₄^[5-7], Fe₂O₃/Al₂O₃^[7-9] and CoO-NiO/YSZ^[10] oxygen carriers have better physicochemical performances. Nevertheless, these oxygen carriers also have disadvantages, such as, low transport capacity for oxygen, insufficient recyclability, expensive cost, low operation temperature or low dispersion degree of metal oxides in inert carriers. Thus metallic oxygen carriers need further research. In addition, Zheng et al^[11] studied the feasibility of a two-step oxidation/reduction reaction between a nonmetallic oxygen carrier, CaSO₄, and a gaseous fuel, in which some key issues such as reaction mechanism and recycling ability are not clear at present.

NiO/NiAl₂O₄^[5-7] oxygen carrier, which is capable of bearing high operation temperature, above 1200°C, attracts wide attention. However, NiO/NiAl₂O₄ prepared by the dissolution method^[5] has low oxidation/reduction conversion ratios. NiO/NiAl₂O₄ prepared by the spray-drying method^[6] needs a long time to reach high oxidation/reduction conversion ratios. NiO/NiAl₂O₄ prepared by the freeze-granulation method^[7] has low mechanism strength. In fact, the sol-gel method is widely used to prepare inorganic materials. In the sol-gel method, solutions of metallic organic/inorganic compounds are used as precursors. After hydrolysis and condensation reactions, colloidal suspension is generated, and then it is solidified to gel. Finally oxygen carriers or other solid compounds are gained through thermal treatment^[12]. The sol-gel method has advantages of good dispersion degree, controllable microstructure, low temperature of thermal treatment, accurate stoichiometry, high purity, and so on. Little reference on NiO/NiAl₂O₄ oxygen carriers prepared by sol-gel method in CLC is available. In this study, NiO/NiAl₂O₄ oxygen carriers are prepared by the sol-gel method. The feasibility of cyclic oxidation/reduction reactions with gaseous fuel (CH₄) is studied. The physicochemical properties and recyclability of

the NiO/NiAl₂O₄ oxygen carriers are characterized.

1 Experimental

1.1 Preparation of NiO/NiAl₂O₄ oxygen carriers

The preparation process of inorganic materials by sol-gel mainly includes the following five key steps: (1) preparation of homogeneous solution; (2) preparation of sol; (3) gelatin process of sol; (4) drying of the wet gel; (5) thermal treatment of the dry gel. The sol-gel process is shown in Fig. 1.

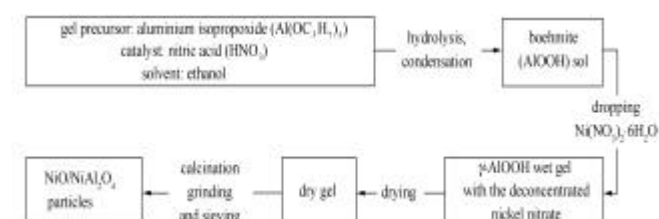


Fig. 1 Process of alkoxide sol-gel method

Chemically pure aluminium isopropoxide (Al(OC₃H₇)₃, from the Chengdu Kelong Chemical Reagent Factory) was selected as the metallic alkoxide, and nitric acid (HNO₃, analytically pure, 65–68%, from the Wuhan Chemical Reagent Factory) was used as a solvent. Aluminium isopropoxide, nitric acid, and distilled water were mixed according to the prescribed ratio, and hydrolytic reaction occurred at an appropriate temperature, thus boehmite (γ-AlOOH) sol was gained. The detailed experimental processes were described as follows: (1) a three-neck flask, a ball reflux condenser tube, a thermometer, a thermostatic magnetic stirring apparatus, a motor stirrer, and other chemical apparatuses were used to build the preparation equipment; (2) 400 mL distilled water was added into the three-neck flask and dimethyl silicone (analytically pure, from the Tianjin Dengfeng Chemical Reagent Factory) was added into a bath container. Next the motor stirrer and the reflux condenser tube, as well as the thermostatic magnetic stirring apparatus were turned on, for heating; (3) the stoichiometric ratio of H₂O and Al(OC₃H₇)₃ was set at 100:1 in this preparation. The porphyzied Al(OC₃H₇)₃ particles (chemically pure) of 45.386 g and the solvent HNO₃ with concentration of 1 mol/L were prepared for the next step; (4) when the temperature of distilled water in the three-neck flask reached 85°C, it was kept constant and then Al(OC₃H₇)₃ was slowly added into the water when it started to hydrolyze. After the hydrolysis reaction of 1.5 h, agglomerated γ-AlOOH particles were generated, which resulted in a milky white hydrolytic solution; (5) the hydrolytic solution was heated to 90°C, and then kept constant; the reflux condenser tube was removed and the three-neck flask was open to air

for 0.5 h, to eliminate the C_3H_7OH from the previous hydrolysis of $Al(OC_3H_7)_3$, and to help complete the hydrolysis of $Al(OC_3H_7)_3$; (6) after the evaporation process, the reflux condenser tube was moved back; 16 mL HNO_3 of 1 mol/L with H^+/Al^{3+} ratio of 0.07 was dropped into the three-neck flask; the agglomerated $\gamma-AlOOH$ particles redispersed into the $\gamma-AlOOH$ sol; (7) the preliminary $\gamma-AlOOH$ sol was prepared using the above steps. It was then left to hydrolyze and age for 12 h at $90^\circ C$; (8) after the ageing process, the reflux condenser tube was removed again and the three-neck flask was open to air for 0.5 h, to eliminate C_3H_7OH from the hydrolysis of $Al(OC_3H_7)_3$. So far, the steady and transparent $\gamma-AlOOH$ sol was obtained.

The next step is to prepare $\gamma-AlOOH$ wet gel with the dispersed nickel nitrate $Ni(NO_3)_2$. The detailed steps are described as follows: (1) The nickel nitrate solution ($Ni(NO_3)_2 \cdot 6H_2O$, analytically pure, from the Tianjin Bodi Chemical Co. Ltd.; the concentration depends on the required NiO amount of coating) is added into distilled water, where $Ni(NO_3)_2$ is in the ionic form; (2) The temperature of the $\gamma-AlOOH$ sol is kept at $90^\circ C$, the reflux condenser tube is moved back again and the prepared nickel nitrate solution is dropped into the three-neck flask, as the rate of the motor stirrer is increased. Thus the sol turns gradually into the wet gel; (3) After the dropping process the resultant green wet gel is stirred for 0.5 h to reach a good dispersion condition.

The last step is the preparation of $NiO/NiAl_2O_4$ particles. The detailed processes are as follows: (1) The wet gel is dried for 36 h at $85^\circ C$ in a beaker placed in a blast drying oven for 5 h at $100^\circ C$ in arks. When the volume of the wet gel decreases a great deal, it is then dried for 5 h at $150^\circ C$ and 5 h at $200^\circ C$. The stepwise drying is to avoid the breakage of the derived low-intensity, light-grayish-green xerogel ($Ni(OH)_2/Al_2O_3$); (2) The $Ni(OH)_2/Al_2O_3$ pieces are then calcined in a electric muffle furnace for 3 h at $450^\circ C$, and for 3 h at $650^\circ C$, step by step. In the calcination process, $Ni(OH)_2$ decomposes into NiO. The resultant faint-yellow NiO/Al_2O_3 pieces perform at a lower intensity than the $Ni(OH)_2/Al_2O_3$ pieces mentioned earlier; (3) The NiO/Al_2O_3 pieces are calcined in the electric muffle furnace for 6 or 10 h at 1300 or $1400^\circ C$. The resultant yellowish green $NiO/NiAl_2O_4$ pieces perform at a higher intensity than the above-mentioned products; (4) The $NiO/NiAl_2O_4$ pieces are then ground in a miller and sieved through screen sizing methods. Up to now, the derived-sol-gel $NiO/NiAl_2O_4$ particles with sizes of 125–180 μm are obtained.

1.2 Experiment methods

Chemical-looping combustion technology requires oxygen carriers with good reactivity in reduction/oxidation reactions

and enough recyclability. The cyclic chemical reactivity of $NiO/NiAl_2O_4$ oxygen carriers prepared by the sol-gel method (where N6AN1306 is selected) with methane has been carried out in a Thermo 500 TGA from Thermo Cahn Cooperation.

The reaction temperature of TGA is $900^\circ C$. The flux of N_2 is 100 mL/min. The mixture gas of 100 mL/min with 50% CH_4 and 50% N_2 is used as fuel. 100 mL/min air is directly used as oxidation gas. The detailed experimental processes are as follows: (1) The N6AN1306 oxygen carrier particles are added into the pot of TGA. (2) The reaction chamber is swept by feeding inert gas N_2 of 100 mL/min, and then heated up to $900^\circ C$ with rate of $10^\circ C/min$. (3) The fuel gas is fed to allow the reduction reaction between oxygen carriers and CH_4 to occur rapidly. The mass of oxygen carriers sharply decreases. (4) N_2 is introduced to sweep the reaction gas in the TGA. (5) The oxidation gas, air, is introduced to oxidize the metal Ni reduced by CH_4 . The mass of the oxygen carriers rapidly increases to a constant. (6) N_2 is introduced again to sweep the air in TGA. (7) The cyclic reduction/oxidation reaction is repeated five times from step 3 to step 6. (8) The feed gas is switched to N_2 and the heating of TGA chamber is stopped. The residual samples of the N6AN1306 oxygen carriers are characterized.

2 Results and discussion

2.1 Physicochemical characterization of $NiO/NiAl_2O_4$ oxygen carriers

On the basis of the mass contents of NiO, sintering temperatures and sintering times, six $NiO/NiAl_2O_4$ oxygen carriers are prepared and listed in Table 1. The oxygen carriers are analyzed by X'Pert PRO X-ray diffractometer (XRD) using $Cu K\alpha$ radiation from the PANA Company of Netherlands. A ceramic X-ray tube is equipped with a maximum power of 2.2 kW, a maximum voltage of 60 kV, and a maximum current of 55 mA. The samples are scanned from $10-90^\circ$. The surface of the particles is examined by a Sirion200 Emission scanning electron microscope (SEM) from the FEI Company. The pore structure of the oxygen carriers is measured by specific surface area and pore size analyzer (ASAP2000) from the Mike Equipment Company, using the N_2 adsorption-desorption (BET) method.

The specific surface area, the volume inside the pore, and the average pore size of the $NiO/NiAl_2O_4$ oxygen carriers are measured by the BET method. The results are also listed in Table 1. It is found that the specific surface area, the volume inside the pore, and the average pore size of $NiO/NiAl_2O_4$ oxygen carriers decrease obviously along with the sintering time and temperature.

Table 1 Classification and the pore structure of the NiO/NiAl₂O₄ oxygen carriers

Oxygen carrier type	Mass content of NiO /%	Sintering temperature <i>t</i> / ^o C	Sintering time <i>t</i> /h	Specific surface area <i>A</i> /m ² ·g ⁻¹	Volume inside the pore <i>V</i> /cm ³ ·g ⁻¹	Average pore size <i>d</i> /nm
N6AN1306	60	1300	6	2.360	0.025	11.2
N6AN1310	60	1300	10	1.940	0.017	9.9
N6AN1406	60	1400	6	0.729	0.008	8.6
N4AN1306	40	1300	6	3.092	0.034	22.9
N4AN1310	40	1300	10	2.408	0.028	12.1
N4AN1406	40	1400	6	0.679	0.006	6.6

This is because the components in the oxygen carriers move toward the inside pore in the calcination process, resulting in the reduction of interface and densification of the structure. The impetus of the process originates from the surface tension of the porous oxygen carrier particles. Nevertheless, the specific surface area, the volume inside the pore, and the average pore size of the oxygen carriers after calcination are still large enough. The oxygen carriers have a porous structure, which benefits their utilization in chemical-looping combustion. Comparatively speaking, N6AN1306 coats the more effective metal oxides (NiO) and has a higher transport capacity for oxygen. This helps reduce the amount of looping material in a real two-interconnected fluidized bed for CLC to a certain extent. In addition, N6AN1306 also has enough high specific surface area, the volume inside the pore, and the average pore size, and thus has a good combination property.

The pattern and morphology of fresh NiO/NiAl₂O₄ oxygen carriers are analyzed by XRD and SEM. Only the results of the N6AN1306 oxygen carrier are given here because of the limit of space, as shown in Figs. 2 and 3. From the XRD pattern in Fig. 2, there are only two phases of NiO and NiAl₂O₄. In the fresh oxygen carriers with different parameters, no Al₂O₃ phase is observed, which proves that Al₂O₃ and NiO have a thorough reaction that generates NiAl₂O₄ in all the selected calcination conditions.

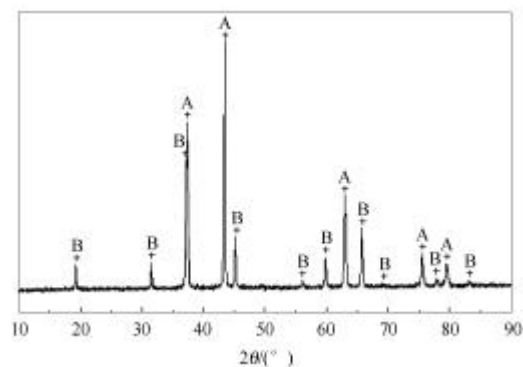


Fig. 2 XRD characterization of the fresh N6AN1306 oxygen carrier

A: NiO; B: NiAl₂O₄

NiAl₂O₄ is an inert carrier, and has no transport capacity for oxygen in the reactions. In addition, SEM shows that fresh N6AN1306 samples are irregular spherical particles with sizes of several hundred micrometers. There are many small holes in the surface, resulting in beehive structure. The porous structure leads to the large specific area of the oxygen carrier particles, which will help increase the chemical reactivity of the oxygen carrier.

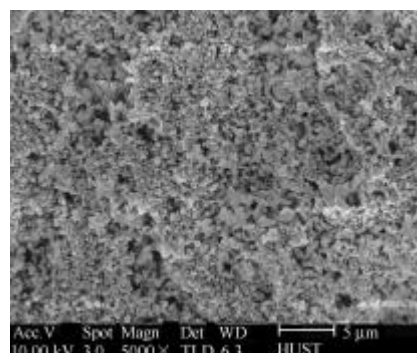


Fig. 3 SEM image of fresh N6AN1306 oxygen carrier

2.2 Cyclic chemical reactivity of the NiO/NiAl₂O₄ oxygen carriers with methane

The cyclic reaction process of the N6AN1306 oxygen carrier with methane/air is shown in Fig. 4.

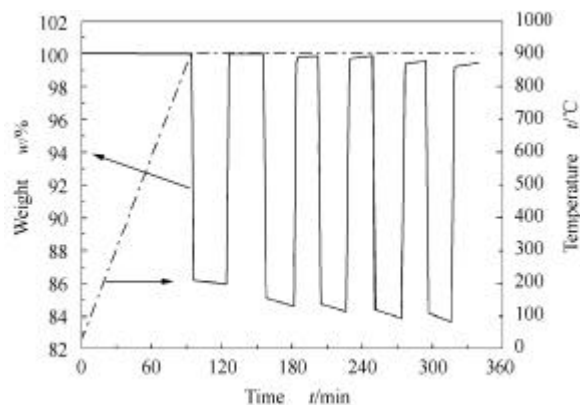


Fig. 4 Weight and temperature data for five cyclics reduction/oxidation reactions of N6AN1306 oxygen carrier with methane/air

Table 2 Weight loss of N6AN1306 oxygen carrier in the five cyclics reduction/oxidation reaction with methane/air

Cycle number	1	2	3	4	5
Mass ratio after one oxidation reaction /%	100.03	99.85	99.89	99.59	99.45
Mass ratio after one reduction reaction /%	85.94	84.60	84.26	83.82	83.62
Difference in mass ratio after one cyclic reaction /%	14.09	15.25	15.63	15.77	15.83

Table 2 shows the history of the maximum mass ratio of the oxygen carrier in the cyclic process. As the circulation proceeds, the reduction degree of the oxygen carriers is gradually intensified. However, the rate of the reduction intensification is gradually alleviated. The reduction enhancement may be ascribed to the formation of a larger inner pore of particles, caused by thermal shock and chemical reaction. On the other hand, the oxidation degree of the oxygen carriers gradually decreases along with the process of the circulation, and the rate of this degradation also decreases gradually. The oxidation degradation may be ascribed to the partial devitalization of the metal Ni, reduced by NiO during the circulation. However, the rate of the oxidation degradation is lower than that of reduction intensification. Hence, the reduction-oxidation reactivity of the oxygen carrier increases by degree on the whole. The cyclic reduction/oxidation reaction between the N6AN1306 oxygen carrier and H_2/air ^[13] also shows that the cyclic reactivity increases by degrees.

The XRD patterns of the N6AN1306 oxygen carrier after the cyclic reaction are shown in Figs. 5 and 6. In Fig. 5, there are three phases: NiO, $NiAl_2O_4$, and the metal Ni after the fifth oxidation reaction. The metal Ni from the reduction reaction is not completely oxidized by the air, which is consistent with the results of Fig. 4.

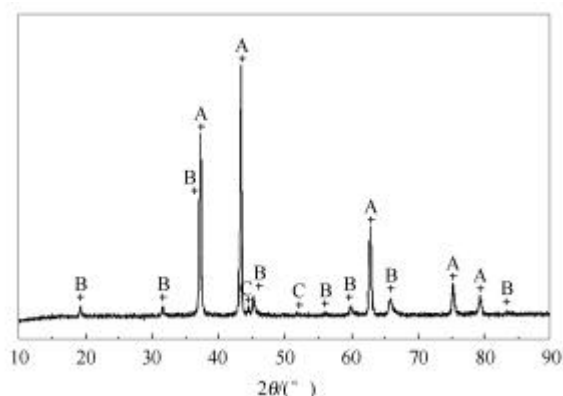
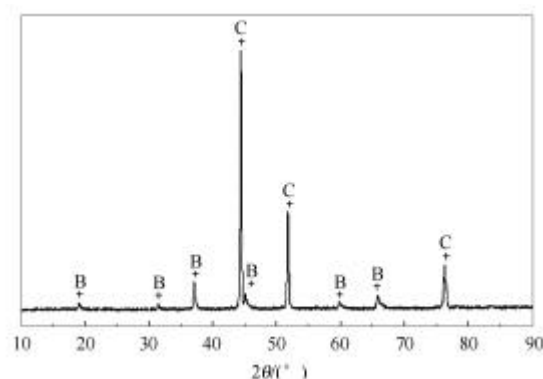
Fig. 5 XRD characterization of the $NiO/NiAl_2O_4$ oxygen carrier after the fifth oxidation reactionA: NiO; B: $NiAl_2O_4$; C: Ni

Figure 6 shows that there are only two phases: $NiAl_2O_4$ and the reduced Ni. There is no NiO after the fifth reduction reaction, which indicates that the active component NiO in the oxygen carrier is completely reduced and the oxygen

carrier has good reduction reactivity.

Fig. 6 XRD characterization of the $NiO/NiAl_2O_4$ oxygen carrier after the fifth reduction reactionsB: $NiAl_2O_4$; C: Ni

The shape and morphology of the N6AN1306 oxygen carrier after five cyclic reactions is shown in Fig. 7. The surface of the fresh oxygen carrier (shown in Fig. 3) is composed of individual grains, in which many micropores exist. However, after the cyclic reactions the diameter of the individual grains increases obviously and the pore size also enlarges remarkably. These results show that sintering behavior appears in the inside of the individual oxygen carrier particle, but the particle still exhibits a porous structure. It is worth noting that the sintering behavior among different particles is not observed after the multiple cyclic reactions.

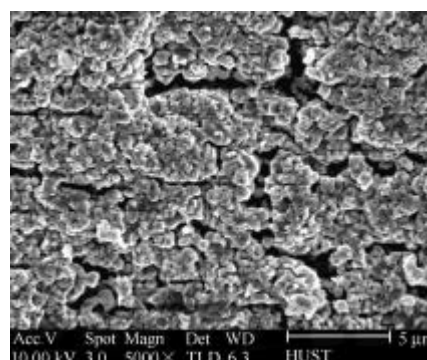


Fig. 7 FSEM image for the N6AN1306 oxygen carrier after five cyclics reaction

The pore structure of the N6AN1306 oxygen carrier particles after multiple cyclic reactions is also analyzed by the BET method. After the five cyclic reactions, the specific

surface area ($1.856 \text{ m}^2/\text{g}$) and the volume inside the pore ($0.021 \text{ cm}^3/\text{g}$) slightly decrease, and the average pore size (13.7424 nm) slightly increases. The change should be ascribed to the internal sintering of the grains. However, the pore structure is still maintained.

3 Conclusions

Six types of $\text{NiO}/\text{NiAl}_2\text{O}_4$ oxygen carriers with different parameters are prepared by the sol-gel method. Based on the physiochemical properties of the oxygen carriers, the optimized preparation parameters are obtained as follows: (1) The hydrolyzation temperature of $\text{Al}(\text{OC}_3\text{H}_7)_3$ is between 85 and 90°C ; (2) The molar ratio of H_2O and $\text{Al}(\text{OC}_3\text{H}_7)_3$ is 100 ; (3) The molar ratio of HNO_3 and $\text{Al}(\text{OC}_3\text{H}_7)_3$ is 0.07 . (4) The wet gel is dried for 36 h at 85°C , and 5 h at 100°C , 5 h at 150°C and 5 h at 200°C , step by step. The stepwise drying benefits the complete drying of the wet gel and avoids breakage on the surface of particles. (5) The dry gel is calcined for 3 h at 450°C , and 3 h at 650°C , and then 6 or 10 h at 1300°C or 1400°C , resulting in oxygen carriers with good mechanism strength.

The cyclic oxidation/reduction reaction of $\text{NiO}/\text{NiAl}_2\text{O}_4$ oxygen carriers with gaseous fuel in a TGA was studied. The feasibility of the sol-gel-derived $\text{NiO}/\text{NiAl}_2\text{O}_4$ oxygen carriers in chemical-looping combustion by gaseous fuel was evaluated. The main conclusions are as follows:

(1) In the five cyclic reactions of the N6AN1306 oxygen carrier with methane/air, the reduction degree of the oxygen carrier is gradually intensified; however, the rate of reduction intensification decreases gradually. On the other hand, the oxidation degree of the oxygen carrier is gradually lowered; however, the rate of the oxidation degradation decreases gradually. Thus the reduction-oxidation reactivity of the oxygen carrier increases by degrees on the whole.

(2) After the five cyclic reactions of the N6AN1306 oxygen carrier with methane/air, the specific surface area and the volume within the pore slightly decrease, however, the average pore size of the oxygen carrier slightly increases. In addition, the oxygen carrier still exhibits a porous structure and the sintering behavior among different particles is not observed.

In conclusion, the results show that $\text{NiO}/\text{NiAl}_2\text{O}_4$ oxygen carriers prepared by the sol-gel method have a good chemical reactivity, good recycle ability, and high bearing temperature of above 900°C , which allows them to be used in chemical-looping combustion by gaseous fuels. Compared with the $\text{NiO}/\text{NiAl}_2\text{O}_4$ oxygen carriers prepared by other methods^[5-7], the sol-gel-derived carrier exhibits a good dispersion degree of active metal oxide, and high specific surface area, volume within the pore, average pore size, and so on, which help update their chemical reactivity. It also has

the advantage of the cyclic reduction/oxidation reactivity gradually increasing. In future studies, the oxidation/reduction mechanism and physiochemical combination properties of the oxygen carriers with different fuels (solid fuels or gaseous fuels) will be studied in TGA, fixed bed reactor and fluidized bed reactor.

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