

Characteristics of the NiO/Hexaaluminate for Chemical Looping Combustion

Kwang Sup Song[†], Yong Seog Seo, Hyung Kee Yoon and Sung June Cho

Catalytic Combustion Research Center, Korea Institute of Energy Research, Daejeon 305-343, Korea

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Abstract—Chemical looping combustion technology has drawn much attention due to advantages such as no NO_x formation and simple CO_2 separation. The thermally stable oxygen carrier in the redox cycle at 1,000-1,400 K is necessary for the chemical looping combustion. The thermally stable hexaaluminate can be a good candidate for the support material of the oxygen carrier. In this work, NiO/hexaaluminate has been developed in order to apply for chemical looping combustion. From the X-ray diffraction patterns, it was found that most of Ni existed in the form of NiO and NiAl_2O_4 in the obtained sample. The NiO supported on NiAl_2O_4 showed good characteristics in the reduction and oxidation reaction. The present work suggested that NiO/hexaaluminate is a promising material as oxygen carrier for the chemical looping combustion.

Key words: Chemical Looping Combustion, NiO, Hexaaluminate, CO_2 Separation, Reduction, Oxidation

INTRODUCTION

Increasing consumption of energy causes the rapid increase of the CO_2 evolution generally coming from combustion of fossil fuel. Because of the potential impact of global climate change, the regulation of CO_2 evolution is an important subject in the world community. One of the promising options for solving this current problem is the separation and isolation of CO_2 from flue gases. To fundamentally solve the current problem of CO_2 separation, Richter and Knoche [1983] introduced new combustion technology utilizing the oxidation and reduction reaction of the metal-oxides. Thereafter chemical-looping combustion was discussed in the literature as an alternative to conventional combustion [Ishida et al., 1987; Anhendsen et al., 1998; Lyngfelt et al., 2001]. The chemical looping combustion system is composed of two fluidized bed reactors, an air reactor and a fuel reactor, as shown in Fig. 1. In this system, the fuel and the combustion air are never mixed. The gases from

the oxidation of the fuel, CO_2 and H_2O leave the only fuel reactor and combustion air is contacted with the metal oxide in the air reactor. Therefore, combustion products of fuel are inherently separated from the other components of the flue gas, i.e., N_2 and unreacted O_2 , and thus no extra energy is needed for this separation. The metal oxide is reduced with gaseous fuel in the fuel reactor. The reduced metal is then transferred to the air reactor where the metal is oxidized with combustion air. So, metal oxides have to get a sufficient reduction and oxidation rate as well as durability. A number of different metals, Ni, Fe and Co, and their corresponding oxides have been investigated [Jin et al., 1999; Mattisson et al., 2001; Jin and Ishida, 2001; Ryu et al., 2001]. Doping of the metal oxides on the supports such as Al_2O_3 , yttria-stabilized zirconium (YSZ), TiO_2 or MgO has also been tested to increase the reactivity and thermal stability or durability of oxygen carriers.

Due to the high thermal stability and catalytic performance, the hexaaluminate has been explored extensively in the catalytic combustion as a promising high temperature combustion catalyst [Machida et al., 1988; Artizzu-Duart et al., 2000; Han et al., 2001]. The formation of hexaaluminate phase by using some additives to alumina provides a high heat resistance against sintering at high temperature. In hexaaluminate having the crystal structure of magnetoplumbite, the crystal growth along the (001) direction is suppressed significantly, resulting in a moderate surface area at high temperature. Some hexaaluminate retained a surface area of ca. $10 \text{ m}^2/\text{g}$ after 5 h of calcination at $1,600^\circ\text{C}$ [Arai and Machida, 1996]. The surface area of hexaaluminate depends on the preparation method. To obtain hexaaluminate of high surface area, sol-gel synthesis is prepared since nano-crystalline phase can be obtained starting from the homogeneously mixed metal alkoxide precursor solution. However, it was reported that the preparation of hexaaluminate by using surfactant is more simple and cost-effective than sol-gel synthesis using metal alkoxide precursor [Cho et al., 2001].

In the present work, the hexaaluminate has been selected as a support in order to improve the thermal stability of oxygen carrier for the chemical looping combustion. The oxygen carrier has been prepared by loading Ni onto hexaaluminate. The sample, NiO/hexa-

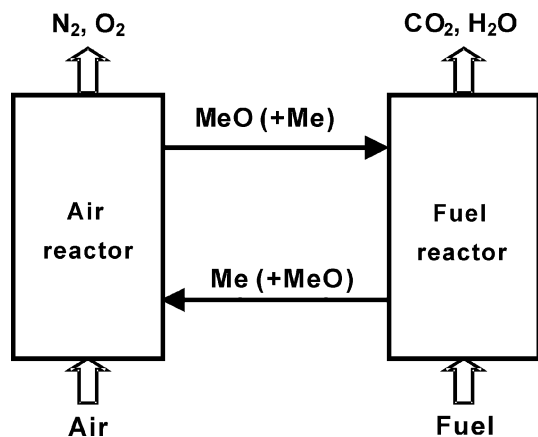


Fig. 1. Schematic diagram of the chemical-looping combustion system (MeO/Me denote recirculated oxygen carrier).

[†]To whom correspondence should be addressed.

E-mail: kssong@kier.re.kr

aluminate, was characterized by X-ray diffractometer, BET surface area and thermo-gravimetric analyzer.

EXPERIMENTAL

Hexaaluminate was prepared by using surfactant such as cetyltrimethylammonium chloride (CTACl), SE-30 [$C_{18}H_{37}(OCH_2CH_2)_{30}OH$] and Triton X-100, according to the procedure used in a previous work [Cho et al., 2001]. The solution of lanthanum acetate, manganese acetate and CTACl was vigorously stirred and then sonicated for 1 h at room temperature. After being aged for 24 h at 100 °C, the solution was dried in an oven at 100 °C. The hexaaluminate powder was obtained by calcining the dried sample in air at 550 °C for 6 h and further at 1,200 °C for 6 h.

NiO/hexaaluminate was prepared by impregnation method. Specified amounts of hexaaluminate were inserted into the $Ni(NO_3)_2$ solution. After being dried at 100 °C for 24 h, the sample was calcined at 1,000 °C for 4 h. The samples of highly loaded Ni (over 30 wt% of Ni) show heterogeneity. To reduce the heterogeneity, the impregnation of Ni was repeated several times by 10 wt%.

The powder X-ray diffraction pattern was obtained by using Cu $K\alpha$ source at 30 kV and 15 mA (Rigaku Miniflex). The surface area of the samples was measured at 77 K by using Micromeritics ASAP

2010. Reduction and oxidation rates were measured with ramping method at a heating rate 10 °C/min by the thermo-gravimetric analyzer (TGA 2950 m, TA instrument). About 20 mg of NiO/hexaaluminate was loaded in a platinum pan and then purified air (>99.99%) was introduced with 100 ml/min for oxidation. After oxidation reaction, the sample was cooled to room temperature under air atmosphere. Reduction reaction was carried out by the changing the reaction gas from air to 5.6% H_2/Ar .

RESULTS AND DISCUSSION

In general, surface area of catalyst plays an important role in the heterogeneous catalytic reaction. Various supports such as alumina and zeolites are used to obtain high surface area of catalyst. Sintering causes the surface area change in the high temperature reaction. So, thermal stability is one of the selection criteria of supports. Recently, it has been revealed that some additives to alumina lead to the formation of a hexaaluminate phase, which possesses a high heat resistance against sintering at high temperature [Arai and Machida, 1996]. Fig. 2 shows X-ray diffraction patterns of the support samples prepared by using surfactant in this study together with alumina. It was found that the hexaaluminate phase was formed after heating the sample at 1,200 °C for 6 h.

To examine the possibility of NiO/ $LaAl_{11}O_{18}$ as oxygen carrier, nickel oxides were loaded onto the hexaaluminate in two different ways, simultaneous and sequential loadings. The surface area of the samples is listed in Table 1. As expected, surface area of oxygen carrier decreased with the Ni content. However, the surface area of oxygen carrier did not change significantly with loading methods.

X-ray diffraction patterns of obtained sample are illustrated in

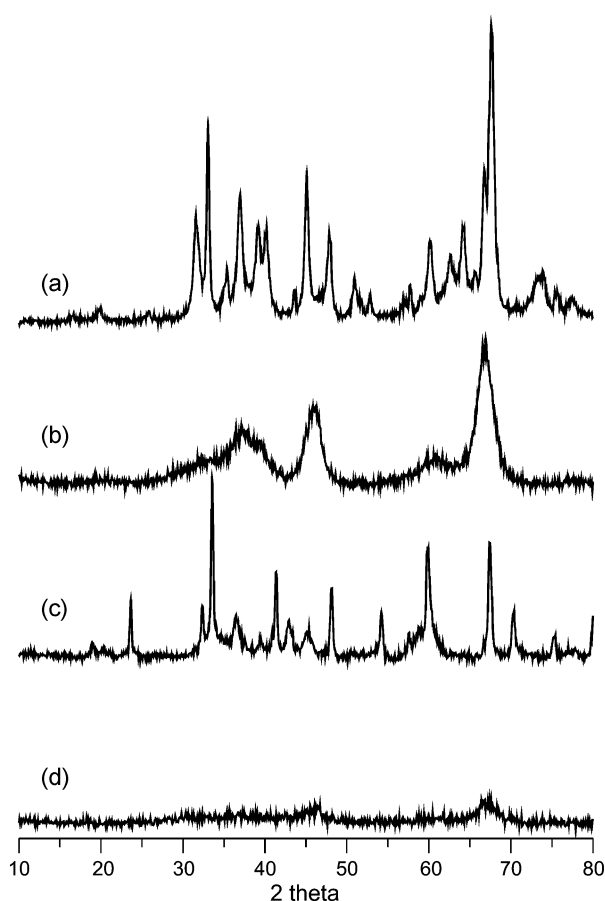


Fig. 2. X-ray diffraction patterns of the thermal stable alumina.

(a) $\gamma-Al_2O_3$ heated at 1,200 °C for 6 h, (b) $\gamma-Al_2O_3$ heated at 600 °C, (c) $LaAl_{11}O_{18}$ heated at 1,200 °C for 6 h, (d) $LaAl_{11}O_{18}$ heated at 600 °C

Table 1. The BET surface area of the samples

Ni fraction	Preparation method	Surface area (m ² /g)
20 wt%	Simultaneous	40.3
30 wt%	Simultaneous	28.5
30 wt%	Sequential	30.2
40 wt%	Simultaneous	24.1
40 wt%	Sequential	21.6

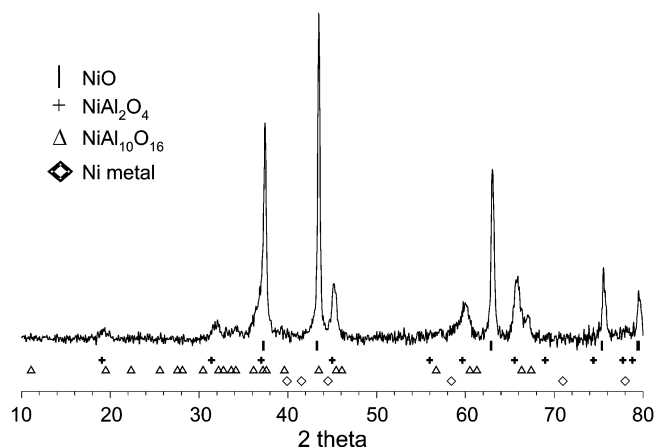


Fig. 3. Characterization of the phase in the sample by X-ray diffraction.

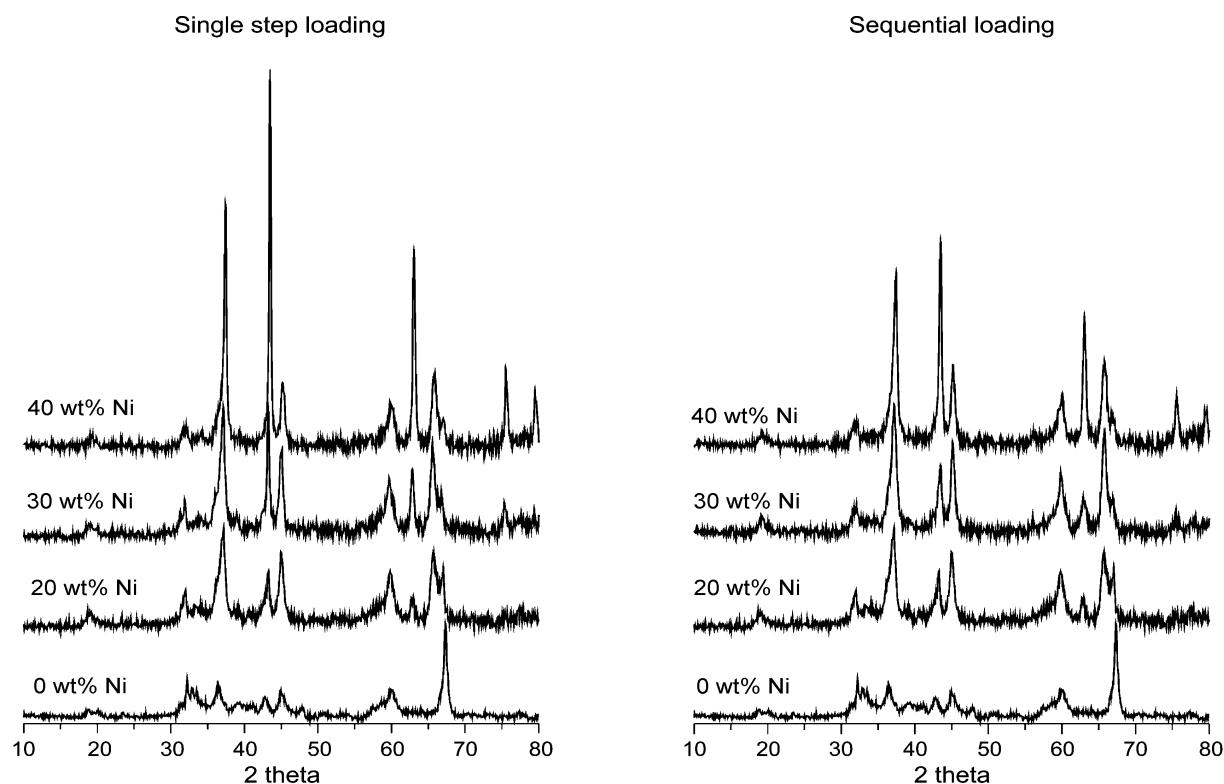


Fig. 4. Change of X-ray diffraction patterns as a function of Ni loading.

Fig. 3. For 40 wt% NiO/LaAl₁₁O₁₈, most of the Ni exists in the form of NiO and NiAl₂O₄. There have been many studies for the oxygen carrier to avoid or suppress the sintering and to increase the reduction/oxidation rate. It was reported that the oxygen carrier, NiO/NiAl₂O₄, significantly improved reaction rate, conversion and regenerability in cyclic reaction due to its interaction between NiO and support, compared with the other materials [Jin et al., 2001]. So, it can be seen that the oxygen carrier prepared by using hexaaluminate is believed to have relatively high reaction rate and physical

strength. To compare the dependence of particle size of Ni phase on loading amount and loading methods, X-ray diffraction patterns of all samples are shown in Fig. 4. As shown in Fig. 4, particle size of NiO increased with the Ni content. Also, the particle size of NiO over the sample prepared by single step loading was larger than that of the sample prepared by sequential loading. Fig. 5 shows the FWHM (full width at half maximum) of the samples. The particle size of NiO is the function of Ni loading and preparation method. From the inspection of color for the samples, it seems that the samples

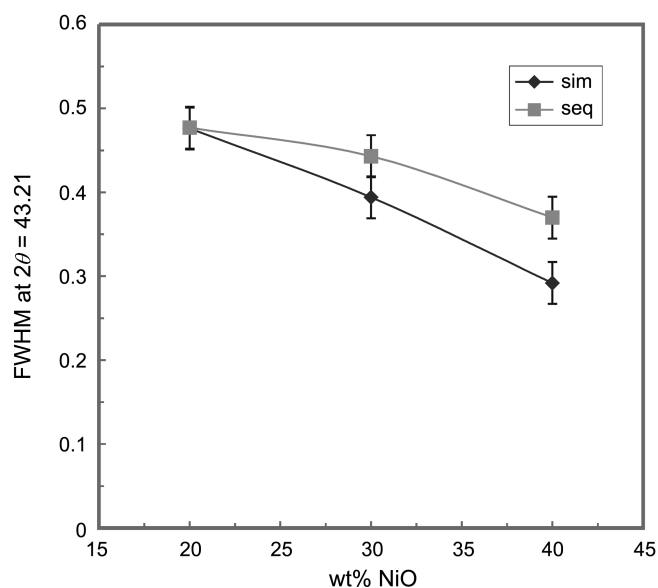


Fig. 5. Estimation of NiO particle size as a function of Ni loading.

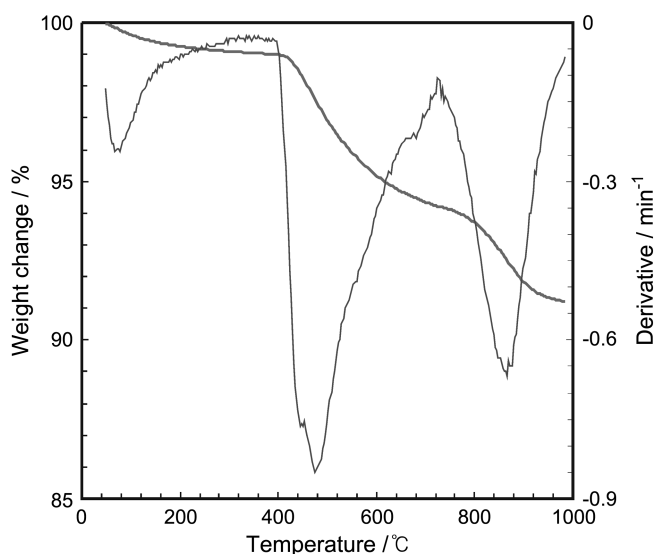


Fig. 6. Weight change of NiO/LaAl₁₁O₁₈ particle in the reducing atmosphere (30 wt% Ni, sequential loading).

Table 2. Analysis for the weight change of NiO/LaAl₁₁O₁₈ in the reducing atmosphere

Ni fraction of the particle	Preparation method	Change of the reduced weight (%)		Weight fraction of Ni (%)	
		Low temp.	High temp.	NiO	NiAl ₂ O ₄
20 wt%	Simultaneous	3.3	2.0	62.2	37.8
30 wt%	Simultaneous	5.2	2.7	65.8	34.2
30 wt%	Sequential	4.8	3.2	60.0	40.0
40 wt%	Simultaneous	7.8	2.3	70.9	29.1
40 wt%	Sequential	8.2	3.0	73.2	26.8

prepared by sequential loading were more homogeneous than the samples prepared by single step loading.

The reduction of NiO by hydrogen for the 30 wt% NiO/LaAl₁₁O₁₈ particle is shown in Fig. 6. As can be seen in this figure, the reduction of nickel oxides takes place in two well-defined temperature ranges. The reduction of the oxygen carrier occurred at first between 400 °C and 700 °C, and the subsequent reduction was followed between 700 °C and 1,000 °C. From the comparison of the TGA results of all samples, the reduction of NiO/LaAl₁₁O₁₈ particle was known to occur in a similar way. Although there was no difference in the reduction temperature windows of the samples, the degree of the reduction depended on the loading amount of NiO over hexaaluminate. Table 2 shows the results of weight change by the reduction of nickel oxides measured from the TGA experiments. Weight change was calculated from the differences of the weights before and after reduction. The increase of the loading amount of nickel over the hexaaluminate resulted in the increase of the weight change at the low temperature but had little effect on the weight change at the high temperature. From the comparison of reduction characteristic for NiO and NiAl₂O₄, it is known that the weight change at the low temperature causes by the reduction of NiO [Jin et al., 1999]. Therefore, it can be said that the increase of the loading amount of nickel over the hexaaluminate affects only the NiO fraction. It is also indicated that the formation of spinel (NiAl₂O₄) between the nickel and the aluminum oxides only occurs on the surface of the

hexaaluminate. It means that the hexaaluminate might have played an important role on inhibiting the sintering of the NiO.

Fig. 7 shows the oxidation reaction characteristics of the reduced sample (Ni/LaAl₁₁O₁₈). Although the reduction of NiO took place in two steps, oxidation of reduced samples occurred in a single step at lower temperature than that of reduction. From the non-isothermal cyclic test for the oxygen carrier by the TGA, it is found that the reduction/oxidation temperatures of Ni are always the same with original sample.

CONCLUSIONS

The novel oxygen carrier for the chemical looping combustion, NiO/LaAl₁₁O₁₈, was prepared by loading Ni onto the hexaaluminate having high thermal stability. It can be seen that the stepwise preparation is more effective to obtain the homogeneous and high dispersion of Ni on the support. From the X-ray diffraction patterns, most of the Ni existed in the form of NiO and NiAl₂O₄. The NiO fraction of the samples was found to increase with loading amount of the Ni on the hexaaluminate. NiO/hexaaluminate prepared in this work showed good reduction and oxidation properties for the application in chemical looping combustion.

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REFERENCES

- Anheden, M. and Svedberg, G., "Exergy Analysis of Chemical Looping Combustion Systems," *Energy Conversion and Management*, **39**, 1967 (1998).
- Arai, H. and Machida, M., "Thermal Stabilization of Catalyst Supports and their Application to High Temperature Catalytic Combustion," *Appl. Catal. A: General*, **138**, 161 (1996).
- Artizzu-Duart, P., Millet, J. M., Guilhaume, N., Gabowski, E. and Primet, M., "Catalytic Combustion of Methane in Substituted Barium Hexaaluminates," *Catal. Today*, **29**, 163 (2000).
- Cho, S. J., Seo, Y. S., Song, K. S., Jeong, N. J. and Kang, S. K., "Surfactant-Mediated Synthesis of Metal Substituted Hexaaluminate from Alumina Sol," *Appl. Catal. B: Environ.*, **30**, 351 (2001).
- Han, M. H., Ahn, Y. S., Kim, S. K., Shon, S. K., Kang, S. K. and Cho, S. J., "Synthesis of Manganese Substituted Hexaaluminate and its Fabrication into Monolithic Honeycomb for Catalytic Combustion,"

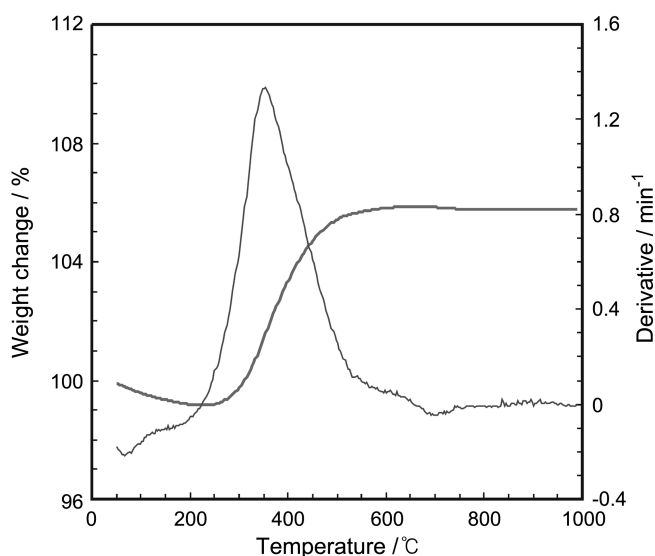


Fig. 7. Weight change of NiO/LaAl₁₁O₁₈ particle in the oxidizing atmosphere (30 wt% Ni, sequential loading).

- Mat. Sci. Eng.*, **A302**, 286 (2001).
- Ishida, A. M., Zheng, D. and Akehata, T., "Evaluation of a Chemical Looping Combustion Power Generation System by Graphic Exergy Analysis," *Energy*, **12**, 147 (1987).
- Jin, H. and Ishida, M., "Reactivity Study on a Novel Hydrogen Fueled Chemical Looping Combustion," *Int. J. Hydrogen Energy*, **26**, 889 (2001).
- Jin, H., Okamoto, T. and Ishida, M., "Development of a Novel Chemical Looping Combustion: Synthesis of a Solid Looping Material of NiO/NiAl₂O₄," *Ind. Eng. Chem. Research*, **38**, 126 (1999).
- Lyngfelt, A., Leckner, B. and Mattisson, T., "A Fluidized-bed Combustion Process with Inherent CO₂ Separation; Application of Chemical-Looping Combustion," *Chem. Eng. Sci.*, **56**, 3101 (2001).
- Machida, M., Eguchi, K. and Arai, H., "Preparation and Characterization of Large Surface Area BaO·6Al₂O₃," *Bull. Chem. Soc. Jpn.*, **61**, 3659 (1988).
- Mattisson, T., Lyngfelt, A. and Cho, P., "The Use of Iron Oxide as an Oxygen Carrier in Chemical-Looping Combustion of Methane with Inherent Separation of CO₂," *Fuel*, **80**, 1953 (2001).
- Richter, H. J. and Knoche, K. F., "Reversibility of Combustion Process," ACS Symposium series, R. A. Gaggioli, ed., Washington, D.C., **235**, 71 (1983).
- Ryu, H. J., Bae, D. H., Han, K. H., Lee, S. Y., Jin, G. T. and Cho, J. H., "Oxidation and Reduction Characteristics of Oxygen Carrier Particles and Reaction Kinetics by Unreacted Core Model," *Korean J. Chem. Eng.*, **18**, 831 (2001).