

Effect of Temperature on Reduction Reactivity of Oxygen Carrier Particles in a Fixed Bed Chemical-Looping Combustor

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Abstract—In a chemical-looping combustor (CLC), gaseous fuel is oxidized by metal oxide particle, e.g. oxygen carrier, in a reduction reactor (combustor), and the greenhouse gas CO₂ is separated from the exhaust gases during the combustion. In this study, NiO/bentonite particle was examined on the basis of reduction reactivity, carbon deposition during reduction, and NO_x formation during oxidation. Reactivity data for NiO/bentonite particle with methane and air were presented and discussed. During the reduction period, most of the CH₄ are converted to CO₂ with small formation of CO. Reduction reactivity (duration of reduction) of the NiO/bentonite particle increased with temperature, but at higher temperature, it is somewhat decreased. The NiO/bentonite particle tested showed no agglomeration or breakage up to 900 °C, but at 1,000 °C, sintering took place and lumps of particles were formed. Solid carbon was deposited on the oxygen carrier during high conversion region of reduction, i.e., during the end of reduction. It was found that the appropriate temperature for the NiO/bentonite particle is 900 °C for carbon deposition, reaction rate, and duration of reduction. We observed experimentally that NO, NO₂, and N₂O gases are not generated during oxidation.

Key words: Chemical-Looping Combustion, Fixed Bed, Oxygen Carrier Particle, CO₂, NO_x

INTRODUCTION

Increasing amounts of gases such as CO₂, CH₄, CFC, NO_x, and SO_x in the earth's atmosphere bring the risk of enhancing the natural greenhouse effect, leading to changes in climate. Since the major greenhouse gas of relevance is carbon dioxide, it is important to recover it to suppress the greenhouse effect. One of the options to overcome the greenhouse effect is the development of CO₂ capture and separation technologies from the flue gases. However, most of these technologies are both costly and energy intensive [Mimura et al., 1997; Herzog and Drake, 1993]. For example, Herzog and Drake [1993] estimated costs ranging from \$18 to \$72 per cubic meter of CO₂ capture using a variety of processes associated with coal and natural gas combustion. Herzog et al. [1997] reported energy penalties ranging from 13 to 37% for natural and coal-fired power plants using current technology and from 9 to 15% using technology anticipated to be available in the future. To solve these problems, chemical-looping combustion technology has been developed since Richter and Knoche [1983] proposed reversible combustion, which utilizes oxidation and reduction of metal.

The chemical-looping combustor consists of two reactors, an oxidation reactor and a reduction reactor. The fuel and air go through different reactors. Fig. 1 and Eq. (1) and (2) illustrate a basic concept of a chemical-looping combustion (CLC) system. The fuel such as CH₄, H₂, CO or C_nH_{2n+2} reacts with metal oxide, NiO, CoO, CuO or Fe₂O₃ for example, in the reduction reactor according to Eq. (2), releasing water vapor and carbon dioxide from the top and metal particles (M) from the bottom. The solid product, metal particles, are transported to the oxidation reactor and react with oxygen in air

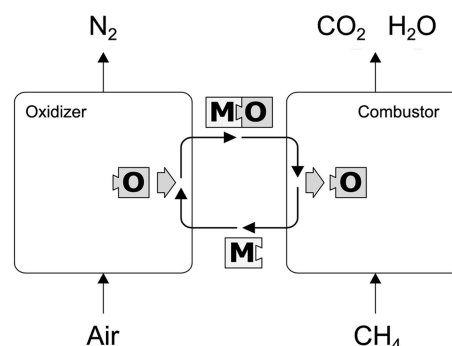


Fig. 1. Chemical-looping combustion system.

in the oxidation reactor according to Eq. (1), producing high-temperature flue gas and metal oxide particles. Metal oxide particles at high temperature are again introduced to reduction reactor and supply the heat required for the reduction reaction. Between the two reactors, metal (or metal oxide) particles play an important role in the transfer of oxygen and heat therefore the looping material between the two reactors is named an oxygen carrier particle.

Oxidation: exothermic reaction



Reduction: endothermic reaction



It is important that the gas composition of the exhaust gas from the reduction reactor is highly concentrated CO₂ and water vapor. Under that circumstance, CO₂ produced in the reduction reaction

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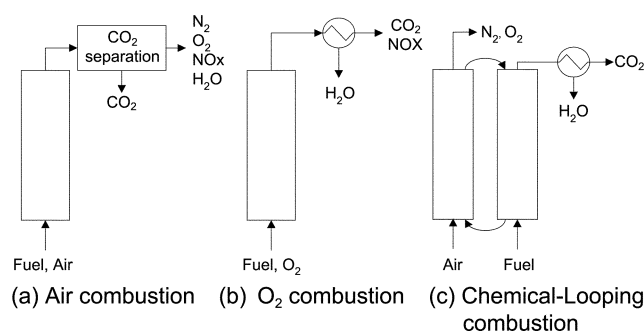


Fig. 2. Comparison between chemical-looping combustion system and other conventional power generation systems.

can be easily recovered by cooling the exhaust gas and removing the liquid water without any extra energy consumption (energy penalty) for CO_2 separation. Another advantage of CLC is that by using this combustor, NO_x formation can be thoroughly eradicated. Oxidation in chemical-looping combustor occurs at considerably lower temperature ($\sim 900^\circ\text{C}$) without flame; thus there is no thermal NO_x formation [Podolski et al., 1995; Jin et al., 1998].

The thermal efficiency of chemical-looping combustion system is very high. According to the previous reports [Copeland et al., 2000; Anheden and Svedevarg, 1996, 1998], efficiency of NGCC (natural gas combined cycle) system shows higher value than those of PF+FGD (pulverised fuel with flue gas desulfurization) system, IGCC (integrated gasification combined cycle) system, and O_2/CO_2 recycle system on the basis of 500 MW electric power plant [IEA Greenhouse Gas R&D Programme Reports]. Wolf et al. [2001] also reported that LNG fueled chemical-looping combustor achieves a thermal efficiency between 52-53% and 5 percent point more efficient than NGCC system with state-of-the-art technologies for CO_2 capture.

Fig. 2 compares the concept of LNG-fueled power generation systems such as air combustion, oxygen combustion, and chemical-looping combustion. As shown in the figure, in the air combustion system, nitrogen in the air contacts with flame and generates thermal NO_x . Moreover, there are many components in the exhaust gas such as N_2 , O_2 , NO_x , H_2O , and CO_2 . Therefore, it is difficult to separate and recover the carbon dioxide and it is a high cost process. To overcome these disadvantages, oxygen combustion system was developed. The composition of the exhaust gas from oxygen combustion system is only CO_2 and water vapor and CO_2 can be easily recovered by cooling the exhaust gas. However, air separation cost is very high and, if oxygen contains some nitrogen, the most parts of nitrogen will be converted to NO_x by contacting with flame at high-temperature condition. But, in the chemical-looping combustion system, oxidation and reduction occur in the separated two reactors, and oxidation occurs at considerably lower temperature ($\sim 900^\circ\text{C}$) without flame; therefore, there is no thermal NO_x formation. The composition of the exhaust gas from the reduction reactor is only CO_2 and water vapor and CO_2 can be recovered by cooling the exhaust gas. And the composition of the exhaust gas from the oxidation reactor is only N_2 and O_2 .

Several research teams such as Japan, Sweden, USA, Norway, and Korea have developed chemical-looping combustion technology. The previous research results on a chemical-looping combustion

system were summarized in the report of Ryu [2003]. Researches on the novel concept of indirect combustion of gaseous fuel and economic efficiency analysis of chemical-looping combustion system have been performed since 1986. The development of oxygen carrier particles and investigations concerning the reactivity of oxygen carrier particles have been conducted since 1994. However, previous results concentrated on improvement of oxygen carrier particle reactivity, and reactivity tests of oxygen carrier particles were mostly performed in a TGA (thermo-gravimetric analyzer). Moreover, most of the reactivity data during reduction were obtained with hydrogen as the reducing gas, and only limited data were obtained with methane as the reducing gas. In order to clearly understand the reaction characteristics of oxygen carrier particles, it is necessary to analyze the gas concentration of exhaust gases from oxidation and reduction reactors. Above all, confirmation of no NO_x emission in the oxidation reactor and measurement of CO_2 selectivity (volumetric ratio of CO_2 to exhaust gases) in the reduction reactor are prerequisite for applying chemical-looping combustion to commercial plants.

In this paper, we made NiO/bentonite particle as an oxygen carrier particle and investigated the effect of reaction temperature on reduction reactivity in a fixed bed reactor by measuring exhaust gas concentration. We also measured NO, NO_2 and N_2O concentration to clarify whether NO_x is formed during oxidation.

EXPERIMENTAL

1. Solid Looping Material

Nickel oxide and bentonite powder were used to prepare the oxygen carrier particles. Their average diameters were 1.7 and $3.7\ \mu\text{m}$, respectively. First, these two powders were mixed by mechanical agitator (NiO and bentonite at the weight ratio of 3 : 2). In the previous study, we pointed out that the NiO particle, which is mixed with bentonite at weight ratio 3 : 2, shows good properties with respect to the reaction rate and maximum conversion [Ryu et al., 2001]. Next, distilled water was added to this powder mixture; the paste obtained was dried at 105°C for 24 hours; and dried material was crushed. Finally, NiO/bentonite particles were calcined in the air at 900°C for 6 hours, and dry sieve analysis was carried out. To measure the NiO weight percent in NiO/bentonite particle, particle den-

Table 1. Reaction conditions and properties of oxygen carrier particles

Gases	
Reduction	CH_4 13%, 2.3 l/min (CH_4 0.3 l/min + N_2 2.0 l/min)
Oxidation	O_2 8.6%, 2.2 l/min (Air 0.9 l/min + N_2 1.3 l/min)
Particle	
NiO weight fraction	0.59
Particle diameter	$400\ \mu\text{m}$ ($\sim 500 + 300\ \mu\text{m}$)
Apparent density	$4,080\ \text{kg/m}^3$
Bulk density	$1,407\ \text{kg/m}^3$
Experimental conditions	
Solid weight	40 g ($5.5\ \text{cm}^3$)
Temperature	500, 600, 700, 800, 900, $1,000^\circ\text{C}$

*Bed depth

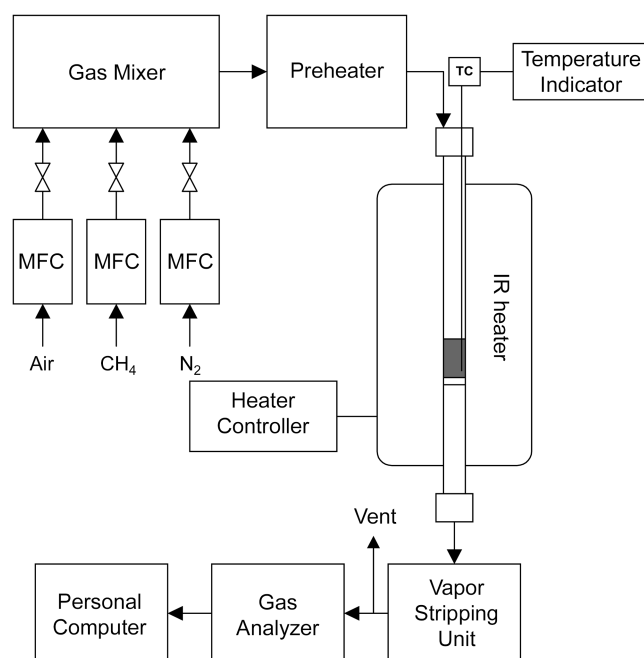


Fig. 3. Experimental set-up.

sity, and porosity, EDAX and mercury porosity measurement were conducted. The properties of NiO/bentonite particles are listed in Table 1.

2. Experimental Apparatus and Methods

The reactivity of NiO/bentonite particle was measured in a fixed bed reactor. Fig. 3 shows a schematic diagram of the fixed bed reactor. The reactor has a length of 0.7 m, with a stainless steel mesh and porous filter of 0.025 m in diameter about 0.43 m from the top. The reaction temperature was measured by K-type thermocouple installed just above the oxygen carrier particle. IR-heater and controller were used to control reaction temperature of fixed bed reactor. The reactant gases, CH₄ and air, as well as inert gas, N₂ were led from the gas cylinder through mass flow controllers (Brooks 5850) and pre-heater to three four-way valves. The outlet gas from the reactor was led through a heated tube to vapor stripping unit (condenser) where H₂O was condensed. The incondensable gases were further led to a gas analyzer (Hartman & Braun Co., Advance Optima) where the concentrations of O₂, N₂O, NO, NO₂, CO, CO₂, and CH₄ were measured with 1-minute intervals.

The NiO/bentonite particle was heated in the reactor to the desired temperature in a flow of nitrogen. After the temperature was stabilized, the experiment was initiated by exposing the oxygen carrier particle to alternating reducing and oxidizing conditions (CH₄ 300 ml/min+N₂ 2.0 l/min for reduction, Air 900 ml/min+N₂ 1.3 l/min for oxidation). In order to avoid the mixing of methane and air, nitrogen was introduced for five minutes after a reducing period. The reaction temperature (500, 600, 700, 800, 900, 1,000 °C) was considered as an experimental variable. Table 1 also lists the main experimental parameters.

RESULTS AND DISCUSSION

Fig. 4 shows the typical gas concentrations of the exhaust gases

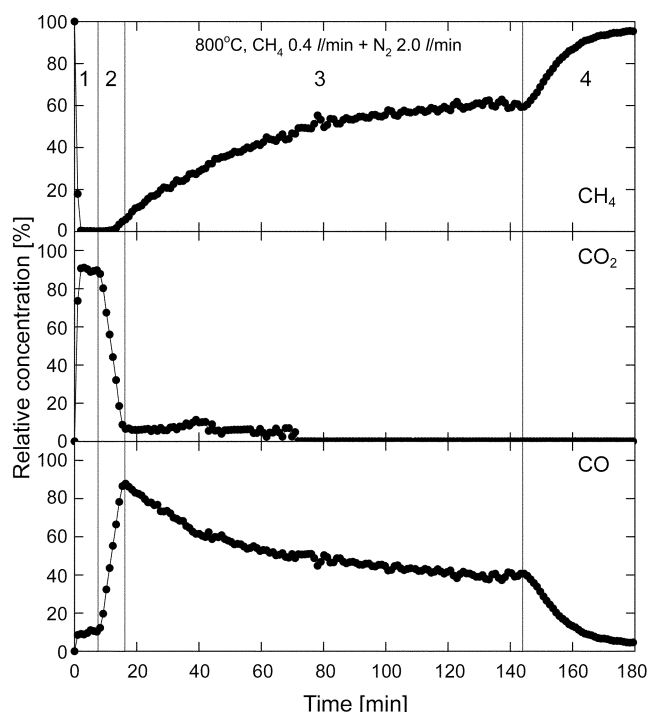


Fig. 4. Typical trend of CH₄, CO₂, and CO concentration with time in the reduction reaction.

as a function of reaction time when NiO/bentonite particle reacted with methane gas. The outlet concentrations of CH₄, CO₂, CO, N₂O, NO, NO₂, and O₂ were measured after condensation of H₂O. In all reduction experiments, only CH₄, CO₂, and CO gases were detected. The ordinate of Fig. 4 represents the relative concentration of each component in the reduction outlet gas and is defined as in Eq. (3), where C_i (i=CH₄, CO₂, CO) is the outlet concentrations of gas component i.

$$\gamma_{red} = \frac{C_i}{C_{CH_4} + C_{CO_2} + C_{CO}} \times 100 \quad (3)$$

The reduction process could be classified into four distinctive periods depending upon the concentration of each component. At the beginning of reduction, in period 1, the concentration of CH₄ dramatically falls. CH₄ reacts with NiO, and CO₂ and CO are generated. The concentrations of CO₂ and CO are maintained virtually constant. We also observed that the concentration of CO₂ gas was much higher than that of CO, namely, most of the CH₄ was converted to CO₂. Next, in period 2, CO₂ concentration is decreased and CO concentration is increased sharply with time because the concentration of oxygen in the NiO/bentonite particle is not sufficient enough to convert CH₄ to CO₂. However, in this period, the concentration of CH₄ is maintained at very low level. Then, in period 3, the oxygen in the NiO/bentonite particle is almost completely exhausted and most of methane is converted to CO. From period 3, the concentration of CH₄ is increased as the reduction proceeds. In this period the concentrations of CO and CO₂ are decreased as the reduction proceeds. Finally, in period 4, CO concentration is decreased but CH₄ concentration is increased rapidly with time due to the lack of oxygen in the NiO/bentonite particle.

If a hydrocarbon fuel is exposed to a high temperature, solid car-

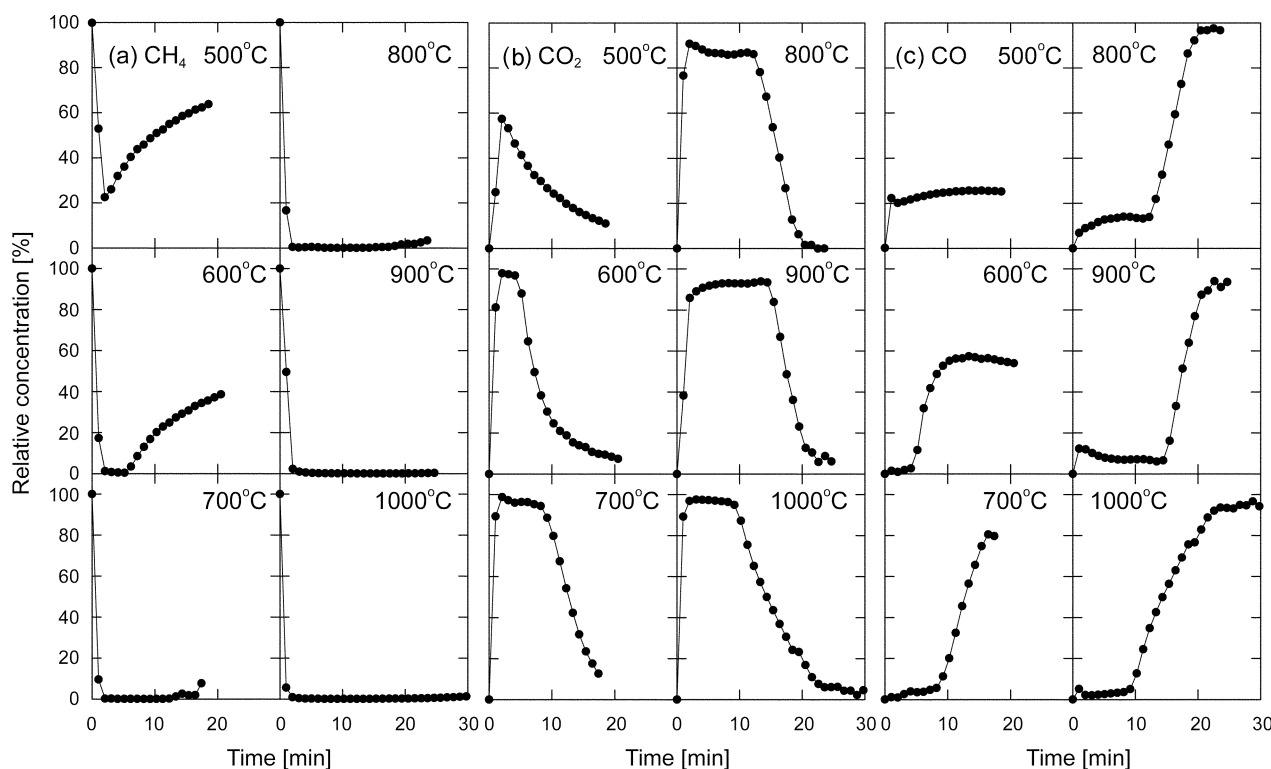


Fig. 5. CH_4 , CO_2 , and CO concentration with time at different reduction temperatures.

bon may form through a number of reactions. The carbon deposition on the solid metal is a fatal problem because it lowers solid reactivity and shortens its life [Lee and Ihm, 1989; Yun and Kim, 1995; Gallado et al., 1998]. Clearly, it is important that significant carbon formation should be avoided in the reduction reactor of a CLC system. Carbon deposition is caused by reaction (4) from the period 2 [Ryu et al., 2003]. Therefore, to suppress further carbon deposition, we switched input gas from methane to nitrogen after period 2.



Fig. 5 shows the concentrations of CH_4 , CO_2 , and CO with time at different reaction temperatures. In Fig. 5(a), the outlet concentration of CH_4 is shown as a function of time at different reaction temperatures. At lower temperature (500°C), the concentration of CH_4 increased after an initial decrease with time, because the reactivity of NiO /bentonite particle is insufficient at low temperature. At higher temperature ($>600^\circ\text{C}$), the concentration of CH_4 is dramatically decreased and maintained at very low level thereafter. Almost all CH_4 reacted to form CO_2 with little or no outlet CO and CH_4 . In Fig. 5(b), the outlet concentration of CO_2 is shown as a function of time. At lower temperature (500°C), the concentration of CO_2 decreased after an initial increase with time. At higher temperature ($>600^\circ\text{C}$), the concentration of CO_2 dramatically increased and was maintained at very high level thereafter. The outlet concentration of CO_2 then decreased again, because oxygen in NiO /bentonite particles is exhausted. In Fig. 5(c), the outlet concentrations of CO are shown as a function of time. As expected, outlet concentration of CO is inversely proportional to that of CO_2 .

In the chemical-looping combustion system, a high conversion

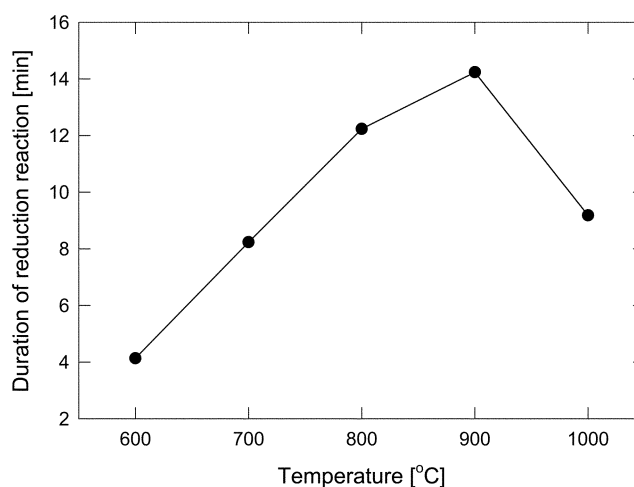


Fig. 6. Effect of temperature on duration of reduction.

of methane to carbon dioxide and water is desired, and this is the best way to avoid carbon deposition. Fig. 6 shows durations of the desirable reduction period, i.e., period 2 in Fig. 4, as a function of reaction temperature. We considered the second period as the best reaction region because during this period almost all CH_4 react to form CO_2 with little or no outlet CO and CH_4 . After this period, the outlet concentration of CO_2 falls, whereas the concentrations of CH_4 and CO rise, and solid carbon may deposit on oxygen carrier particles. As shown in the figure, the duration of period 2 is increased with increasing temperature, but at $1,000^\circ\text{C}$, it is decreased somewhat. These results could be explained by the results obtained in a TGA (see later).

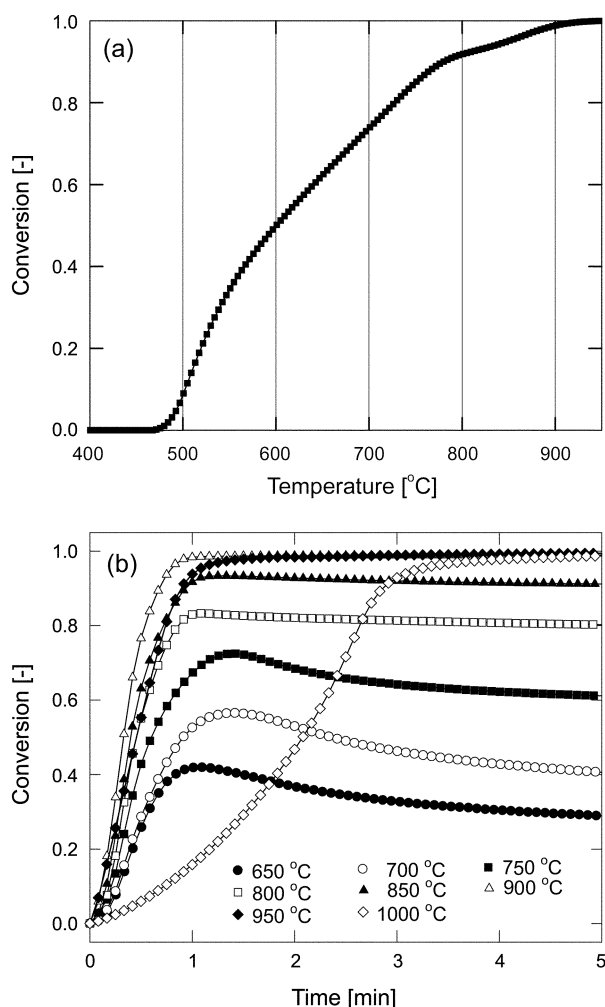


Fig. 7. Effect of temperature on reduction conversion of NiO/bentonite particle (TGA experiments).

(a) non-isothermal reduction by H_2
 (b) isothermal reduction by CH_4

Fig. 7(a) shows the reactivity of the NiO/bentonite particles in a TGA reactor. The average diameter of the NiO/bentonite particle was 128 μm (106–150 μm). Temperature was increased from 50 to 1,000 $^{\circ}C$ at a rate of 5 $^{\circ}C/min$. Hydrogen (13.0%, N_2 balance) was used as reducing gas to avoid deposition of carbon. By using hydrogen as reducing gas, we can observe the effect of temperature on reduction reactivity without carbon deposition. The reduction conversion X is plotted against the reaction temperature (time), where X is defined as in Eq. (5), where W is the actual mass of particles, W_{Ni} is the mass of the particles after complete reduction to Ni/bentonite, and W_{NiO} is the mass of the particles after complete oxidation to NiO/bentonite.

$$X = \frac{W_{NiO} - W}{W_{NiO} - W_{Ni}} \quad (5)$$

Reduction conversion increased with temperature and reduction conversion reached unity about 950 $^{\circ}C$. This result means that the amount of NiO, which could react with reducing gas, is dependent on temperature. To clarify the result that the amount of NiO, which could react with reducing gas, varied with temperature, we also per-

formed isothermal reduction experiments. Fig. 7(b) shows the results of reactivity tests in isothermal conditions (650, 700, 750, 800, 850, 900 $^{\circ}C$). The average diameter of NiO/bentonite particle was 91 μm (75–106 μm). Methane (5.04%, N_2 balance) was used as reducing gas to consider the effect of carbon deposition on maximum conversion. In this figure the reduction conversion X is plotted against the time. It was found that the reduction rates and maximum conversions are strongly dependent on temperature. At lower temperature (650–850 $^{\circ}C$), reduction conversion initially increased by reduction of nickel oxide. After that, the reduction conversion is decreased (particle weight is increased) due to the carbon deposition. These results mean that carbon formation takes place after maximum conversion of particles at each reaction. At higher temperature (900–1,000 $^{\circ}C$), there are no carbon depositions, and conversions are increased up to unity. However, trends of conversion with time for 950 and 1,000 $^{\circ}C$, i.e., slopes of conversion profiles, are quite different from those at lower temperatures since sintering took place and lumps of particles were produced at higher temperature; therefore, the void fraction of particles is decreased, so the reaction rate is decreased [Ishida et al., 1998]. The maximum conversions without carbon deposition increased with increasing temperature. Moreover, the reduction rate increased with increasing temperature up to 900 $^{\circ}C$; after that it decreased with increasing temperature. These results are in line with the result of Fig. 6 and we can conclude that the optimum operating temperature for NiO/bentonite particle is 900 $^{\circ}C$ from the viewpoint of carbon deposition, reaction rate, and duration of reduction.

Fig. 8 shows the typical oxidation reactivity evolved in time in the fixed bed reactor. After the Ni/bentonite particles were produced in the former reduction, they were re-oxidized by air. The outlet concentrations of CH_4 , CO_2 , CO , N_2O , NO , NO_2 , and O_2 were

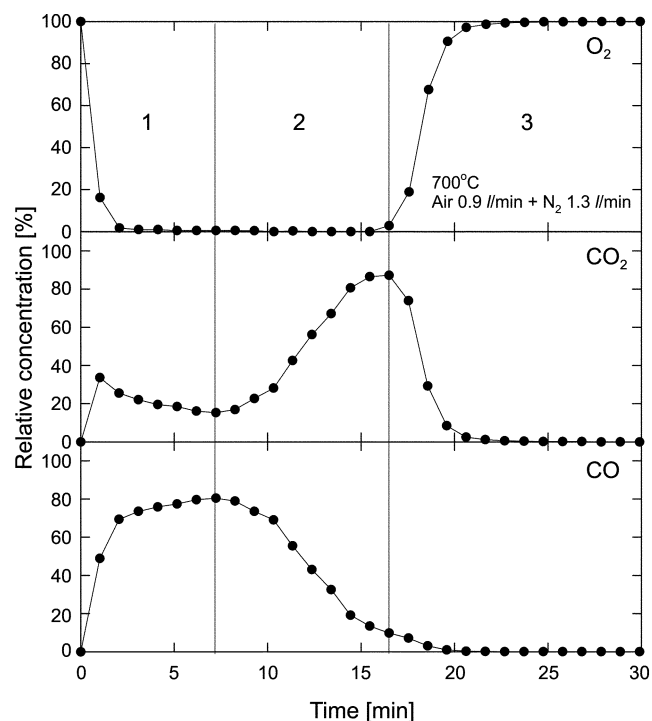


Fig. 8. Typical trends of O_2 , CO_2 , and CO concentration with time in the oxidation reaction.

then measured. We observed that N_2O , NO , and NO_2 gases were not generated in all the oxidation experiments. However, CO_2 and CO gases were detected because deposited carbon during reduction period was oxidized. The ordinate represents the relative concentration of each component in the oxidation outlet gas and defined as in Eq. (6), where C_i , ($i=O_2$, CO_2 , CO) is the outlet concentration of gas component i .

$$\gamma_{i,oxi} = \frac{C_i}{C_{O_2} + C_{CO_2} + C_{CO}} \times 100 \quad (6)$$

Oxidation regime could be classified into three distinctive periods depending upon the concentration of each component. At the beginning of oxidation, period 1 in Fig. 8, the concentration of O_2 dramatically decreased and maintained at very low level. During this period, O_2 reacts with Ni and/or deposited carbon during reduction. If oxygen reacts with deposited carbon, CO_2 and CO gases are generated. We observed that CO_2 and CO gases are generated and the concentration of CO is much higher than that of CO_2 , that is, the oxygen is not enough to oxidize Ni to NiO and to react with deposited carbon, simultaneously. After that, in period 2, CO_2 concentration increased and CO concentration decreased with time. However, in this period, the concentration of O_2 is very low; therefore, we can conclude that most of oxygen is used to react with deposited carbon. Finally, in period 3, the concentrations of CO_2 and CO decreased but O_2 concentration increased rapidly with time because the oxidation of oxygen carrier particle and combustion of deposited carbon are terminated. In oxidation tests of reduced NiO /bentonite particle with methane, deposited carbon reacted with oxygen in the air and produced CO_2 and CO . Therefore, duration of oxidation is dependent on the amount of deposited carbon, and it is difficult to clarify the effect of temperature on oxidation reactivity. In order to investigate oxidation reactivity more clearly, it is necessary to perform reduction of NiO /bentonite particle with hydrogen, i.e., without deposited carbon. However, in all oxidation experiments, no NO_x emission was detected during the oxidation cycle.

CONCLUSIONS

In order to develop a chemical-looping combustor and to obtain the basic reactivity data necessary for the design and operation of a practical reactor, we have experimentally examined the reactivity of the NiO /bentonite particle in a fixed bed reactor. During the reduction period, most of the CH_4 are converted to CO_2 with small formation of CO . Limited formation of carbon on the oxygen carrier particle was detected as indicated by relatively small CO_2 peak and high CO peak in high solid conversion region. However, provided that the chemical-looping combustor is operated within a lower solid conversion range, carbon deposition could be avoided. Reduction reactivity (duration of reduction) increased with temperature but decreased at higher temperature. The NiO /bentonite particle tested showed no agglomeration or breakage up to $900^\circ C$, but at $1,000^\circ C$, sintering took place and particle lumps were formed. It was found that the appropriate temperature for the NiO /bentonite particle is $900^\circ C$ from the viewpoint of carbon deposition, reaction rate, and duration of reduction. No NO_x formation was detected during oxidation. These results support the fact that the NiO /bentonite particle is a suitable material up to $900^\circ C$ and will play an impor-

tant role in the application of the chemical-looping combustion.

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NOMENCLATURE

W	: instantaneous weight of particles [mg]
W_{Ni}	: completely reduced weight of particles [mg]
W_{NiO}	: completely oxidized weight of particles [mg]
X	: conversion [-]
C_{CH_4}	: concentration of CH_4 [ppm]
C_{CO_2}	: concentration of CO_2 [ppm]
C_{CO}	: concentration of CO [ppm]
C_{O_2}	: concentration of O_2 [ppm]

Greek Letters

$\gamma_{i,oxi}$: relative concentration of i component during oxidation [%]
$\gamma_{i,red}$: relative concentration of i component during reduction [%]

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