

Carbon Deposition Characteristics and Regenerative Ability of Oxygen Carrier Particles for Chemical-Looping Combustion

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Abstract—For gaseous fuel combustion with inherent CO₂ capture and low NO_x emission, chemical-looping combustion (CLC) may yield great advantages for the savings of energy to CO₂ separation and suppressing the effect on the environment. In a chemical-looping combustor, fuel is oxidized by metal oxide medium (oxygen carrier particle) in a reduction reactor. Reduced particles are transported to the oxidation reactor and oxidized by air and recycled to the reduction reactor. The fuel and the air are never mixed, and the gases from the reduction reactor, CO₂ and H₂O, leave the system as separate streams. The H₂O can be easily separated by condensation and pure CO₂ is obtained without any loss of energy for separation. In this study, NiO based particles are examined from the viewpoints of reaction kinetics, carbon deposition, and cyclic use (regenerative ability). The purpose of this study is to find appropriate reaction conditions to avoid carbon deposition and achieve high reaction rate (e.g., temperature and maximum carbon deposition-free conversion) and to certify regenerative ability of NiO/bentonite particles. In this study, 5.04% methane was used as fuel and air was used as oxidation gas. The carbon deposition characteristics, reduction kinetics and regenerative ability of oxygen carrier particles were examined by TGA (Thermal Gravimetric Analyzer).

Key words: Chemical-Looping Combustion, Carbon Deposition, Reactivity, Cyclic Test, Regenerative Ability

INTRODUCTION

Advanced thermal power systems such as a combined cycle have been developed, but problems remain in these combustion systems. In a conventional system fuel and air are directly mixed and burned, which gives rise to some problems including environmental problems about emission of carbon dioxide (CO₂), nitrogen oxides (NO_x), and so on [Park et al., 1999]. It is important to recover carbon dioxide for suppressing the greenhouse effect. One of the options to overcome the greenhouse effect is the development of CO₂ capture and separation technologies from flue gases. However, most of these technologies require a large amount of energy to separate and collect CO₂ from the exhaust gas because CO₂ is diluted by N₂ in air in the conventional system. For example, if CO₂ is recovered from the exhaust gas in power plants, it gives rise to the relative decrease of the thermal efficiency from 9-27% and increase in the power generation cost between 1.2 and 2.3 times [Akai et al., 1995; Kimura et al., 1995; Ishida and Jin, 1996]. To resolve these problems, Richter and Knoche [1983] proposed reversible combustion, which utilizes oxidation and reduction of metal, and Ishida et al. [1987] proposed a new-concept combustion method—the chemical-looping combustor (CLC). The concept of this novel combustion is completely different from the traditional one.

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 Eqs. (1) and (2) illustrate a basic concept of a chemical-looping combustion (CLC) system. For exam-

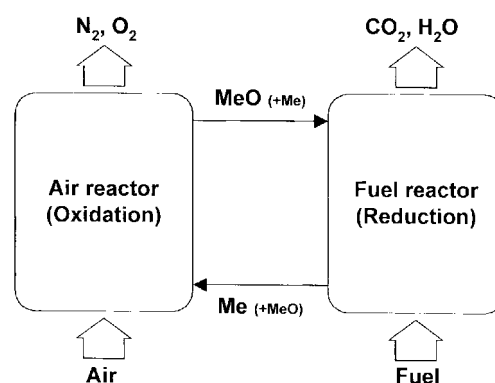
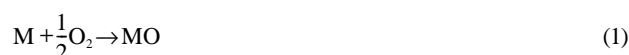


Fig. 1. Conceptual diagram of chemical-looping combustor.

ple, a fuel such as CH₄, H₂, CO or C_nH_{2n+2} reacts with metal oxide, NiO, CoO, CuO or Fe₂O₃ in the reduction reactor according to Eq. (2), releasing water vapor and carbon dioxide from its top and metal particles (M) from its bottom. The solid products, metal particles, are transported to the oxidation reactor and react with oxygen in air 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 the reduction reactor and supply the heat required for the reduction reaction. Between the two reactors, metal (or metal oxide) particles perform the role of transferring oxygen and heat and, therefore, looping material between the two reactors is named as oxygen carrier particle.

Oxidation: exothermic reaction



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^{*}This paper is dedicated to Professor Dong Sup Doh on the occasion of his retirement from Korea University.

Reduction: endothermic reaction



It is important that the gas composition of the exhaust gas from the reduction reactor is only highly concentrated CO_2 and water vapor. For this reason, CO_2 produced in the reduction reaction can easily be recovered by cooling the exhaust gas and removing the condensate liquid water, without any extra energy consumption (energy penalty) for CO_2 separation. One more important issue is that by using this combustor, NO_x formation can be thoroughly eradicated. Nitric oxides are formed in flames by three mechanisms: thermal NO_x , fuel NO_x and prompt NO_x . Fuel NO_x is formed during the combustion of nitrogen-containing fossil fuels and prompt NO_x occurs by the collision and fast reaction of hydrocarbons with molecular nitrogen in fuel-rich flames. However, in a chemical-looping combustor, oxidation of reduced metal takes place without fuel and flame. Therefore, there are no fuel NO_x and prompt NO_x . Moreover, the thermal NO_x mechanism is important in high-temperature flames; for instance, Pershing and Wendt [1977] showed that thermal NO_x becomes significant at temperatures above 1,650 K (1,377 °C). Because oxidation in a chemical-looping combustor occurs at considerably lower temperature (around 900 °C) without flame, there is no thermal NO_x formation [Podolski et al., 1995; Jin et al., 1998]. We observed that no NO_x was generated in our previous experiment [Ryu et al., 2002].

The thermal efficiency of a chemical-looping combustion system is very high. According to previous reports, the efficiency of the NGCC (natural gas combined cycle) system shows higher values than that of PF+FGD (pulverized fuel with flue gas desulfurization) system, IGCC (integrated gasification combined cycle) system and O_2/CO_2 recycle system in the basis of 500 MWe power plant [IEA Greenhouse Gas R&D Programme Reports]. And Wolf et al. [2001] reported that an LNG fueled chemical-looping combustor achieves a thermal efficiency between 52-53% and is 5 percent point more efficient than an NGCC system with state-of-the-art technology for CO_2 capture.

In solid-gas reactions (e.g., catalytic reactions, electrochemical reactions, and hot-gas cleanup), carbon deposition on the solid metal is a fatal problem, because it lowers solid activity and shortens its life [Lee and Ihm, 1989; Yun and Kim, 1995; Gallado et al., 1998]. To avoid carbon deposition, a high concentration of water vapor is usually added (say, $\text{H}_2\text{O}/\text{C} > 1$). In the reforming of fuel, the water vapor is consumed as a reactant during reaction, and hence excess water vapor is required to avoid carbon deposition. In chemical-looping combustion, however, water vapor is produced, instead of consumed, as a reduction product when hydrocarbon or coal gas is used as fuel. It means that reduction in chemical-looping combustion does not require excess water vapor to suppress carbon deposition. This is quite different from the water-consuming reaction, and it is favorable for avoiding carbon deposition [Ishida et al., 1998]. However, in experiments conducted by Ishida et al. [1998] on NiO as an oxygen carrier, carbon was formed under certain conditions. And they calculated the input $\text{H}_2\text{O}/\text{CO}$ ratio to avoid carbon deposition.

In this paper, we have made NiO/bentonite particles, and investigated the effect of temperature on reduction reactivity and carbon deposition behavior to find optimum reaction temperature. Further-

more, we have also examined changes in the reactivity with an increase in the number of cycles of reduction by CH_4 and oxidation by air, since this is an important factor to realize the application of the chemical-looping combustion to the power station and to reduce the cost of the proposed system.

EXPERIMENTAL

1. Preparation of Solid Looping Materials

We used nickel oxide as metal oxide component in reduction reaction. Nickel oxide powder and bentonite powder were used to prepare the particles. Their average diameters were 1.7 and 3.7 μm , respectively. These two kinds of powders were mixed by mechanical agitator (NiO and bentonite at the weight ratio of 3 : 2). In a previous study, we pointed out that NiO particles mixed with bentonite at weight ratio 3 : 2 had good properties with respect to the reaction rate and conversion [Ryu et al., 2001]. Distilled water was added to this powder mixture. Obtained paste was dried at 105 °C for 24 hour. Dried material was crushed. NiO/bentonite particles were calcined in the air at 900 °C for 6 hour, and dry sieve analysis was carried out. To measure the NiO weight percent in NiO/bentonite particles, particle density, and porosity, EDAX and mercury porosity analysis were carried out. The physical properties and NiO weight percent in NiO/bentonite particles are listed in Table 1.

2. Experimental Apparatus and Methods

The reactivity of NiO/bentonite particles was measured by a TGA (thermal gravimetric analyzer). Fig. 2 shows a schematic diagram of the thermal gravimetric analyzer apparatus (TGA 2950, TA Instrument). Temperature range, heating rate range, maximum gas flow rate, and weighing range of TGA 2950 are 25-1,000 °C, 0.1-

Table 1. Properties of NiO/bentonite particles

Particles	NiO/bentonite
NiO weight percent [%]	59
Porosity [%]	69
Particle size [μm]	91 μm (-106+75)
Particle density [kg/m^3]	4,038
Bulk density [kg/m^3]	1,319

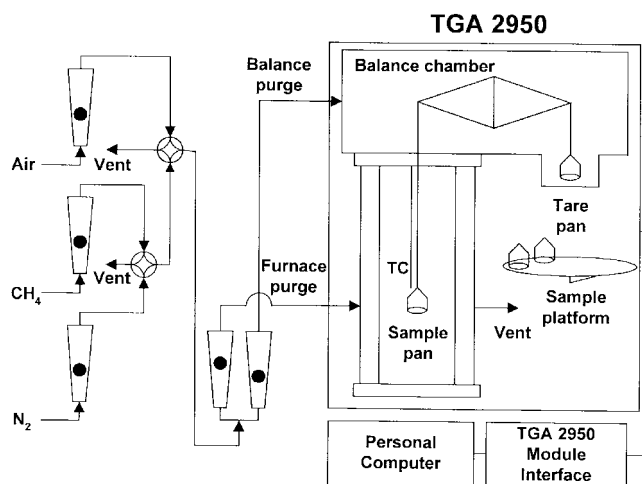


Fig. 2. Schematic diagram of TGA reactor.

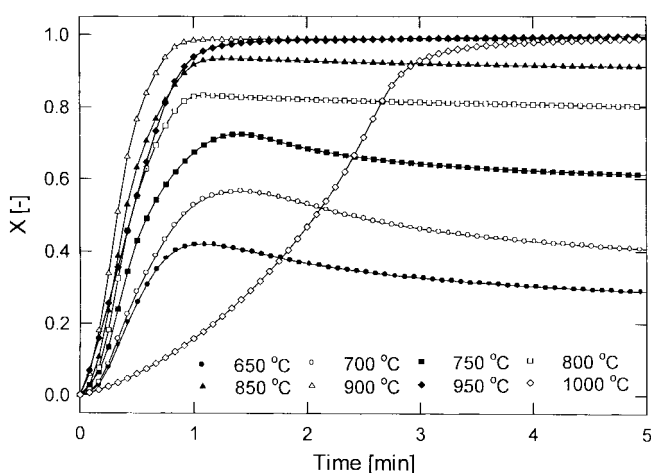
Table 2. Summary of experimental method and variables

Method	Isothermal
Inert gas	N ₂
Reacting gas	Reduction: CH ₄ 5.04%, N ₂ balance Oxidation: Air
Temperature [°C]	650, 700, 750, 800, 850, 900, 950, 1,000
Cyclic test	900 °C, 12 cycle

100 °C/min, 100 ml/min, and 0.1 µg-100 mg or 1-1,000 mg, respectively. The specimen particle was placed on a sample pan situated on the sample arm of the balance. The reactant gases (CH₄ for reduction and air for oxidation) were controlled by float type flow-meter. Inert gas (N₂) was fed into the weighing unit to prevent the reactant gas from diffusing into the balance chamber. When the temperature reached the specified value by use of an electric furnace, four-port switching valves changed the gaseous stream from nitrogen to reactant gas. Weight of the solid particle and the reaction temperature were recorded continuously by a computer. In all experiments the flow rates of the reactant gas (CH₄ 5.04%, N₂ balance) and inert gas (N₂) were set as 100 ml/min (at standard state). The temperature and the number of cycle were considered as experimental variables. Experimental methods and variables are summarized in Table 2.

RESULTS AND DISCUSSION

Fig. 3 shows the dependence of the reduction conversion on temperature for NiO/bentonite particles of 91 µm diameter. The reduction conversion X is plotted against the reaction time, where X is defined as $X = (W_{NiO} - W) / (W_{NiO} - W_{Ni})$, where W is instantaneous weight, W_{Ni} and W_{NiO} are the completely reduced weight and completely oxidized weight (i.e., initial weight), respectively. Therefore, $X=1$ corresponds to the completely reduced state (Ni/bentonite), while $X=0$ to the completely oxidized state (NiO/bentonite). As shown in the figure, it was found that the reduction rate is strongly dependent on temperature. At a low temperature (650-850 °C), reduction conversions initially increased by reduction of nickel oxide

**Fig. 3. Effect of temperature on reduction conversion and carbon deposition.**

(decreasing of weight) according to reaction (3).



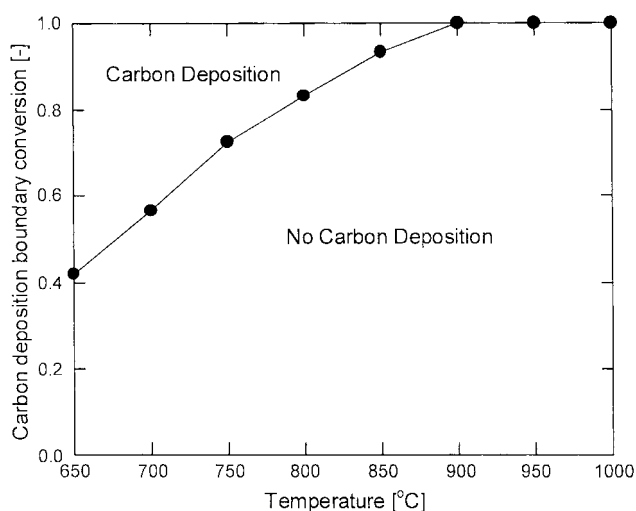
After that, the reduction conversions were decreased due to carbon deposition (increasing of weight) according to reaction (4) or (5) [Ishida et al., 1998]. The carbon deposition rates were decreased with the increased amount of the deposited carbon.



At higher temperature (900, 950, 1,000 °C), there are no carbon depositions and conversions increase up to unity. However, trend of conversion with time for 1,000 °C is quite different from those of lower temperature. Since sintering took place and a lump of particles was produced at higher temperature (950, 1,000 °C), therefore the void fraction of particles decreased and reaction rate decreased [Ishida et al., 1998]. Hence, we consider that a higher temperature is appropriate for chemical-looping combustion to operate without carbon deposition.

Fig. 4 shows the dependence of the carbon deposition on reaction temperature. The carbon deposition boundary conversions are plotted against reaction temperature, where we considered maximum conversion before carbon deposition commencement as carbon deposition boundary conversion. As shown in the figure, carbon depositions decreased with reaction temperature, and at higher temperature (>900 °C) there are no carbon depositions. The line separates the carbon deposition-free region from the carbon-deposited area. The carbon is usually deposited on the catalyst, and so to avoid carbon deposition, water vapor is often added to a reactor. Here, it is particularly noteworthy that carbon deposition can be completely controlled by a simple way, i.e., operating within an appropriate conversion range. That is, if we operate a chemical-looping combustor under the carbon deposition boundary conversion, we can avoid carbon depositions without water (steam) addition and heat loss.

Fig. 5 shows the effect of temperature on reduction rate. As shown, reduction rate decreased after an initial increase with reaction temperature. As we said earlier, at higher temperature (950, 1,000 °C) sintering took place and a lump of particles was produced; there-

**Fig. 4. Carbon deposition regime map.**

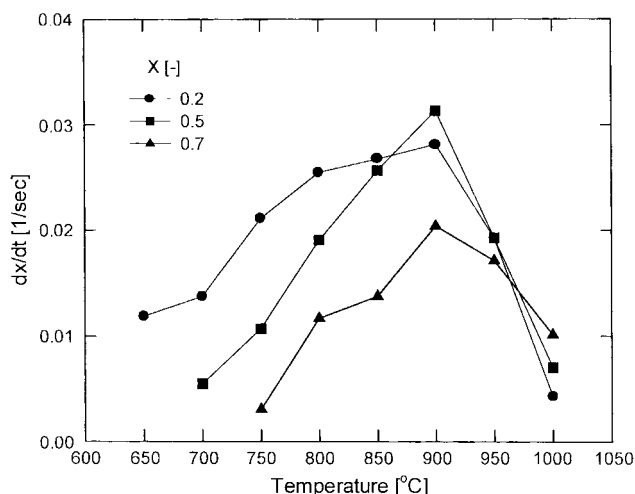


Fig. 5. Effect of temperature on reduction rate.

fore the void fraction of particles decreased and reaction rate decreased [Ishida et al., 1998]. For all conversions, reduction rates show maximum values at 900 °C. Hence, we consider that 900 °C is the optimum temperature for chemical-looping combustion with NiO/bentonite particles. Accordingly, from the viewpoints of reduction kinetics and the resistance against carbon deposition, the appropriate temperature was found to be 900 °C.

Regenerative ability is one of the important problems for application of chemical-looping combustion to commercial plants. The regenerative ability of the looping material was examined at 900 °C. As we said earlier, 900 °C is the optimum temperature to avoid carbon deposition and achieve high reaction rate. Fig. 6(a) shows weight change of NiO/bentonite particles with time in cyclic reduction and oxidation. Fig. 6(b) is a detailed drawing for the first cycle. As shown in the figure, particle weight initially decreased by fast reduction of oxygen carrier (from NiO to Ni). After reduction of each cycle, the oxidation was also very fast and the final weights of oxidation returned to the initial ones by oxidation of oxygen carrier (from Ni to NiO). However, from the second cycle, carbon deposition took place and particle weight increased before oxidation reaction.

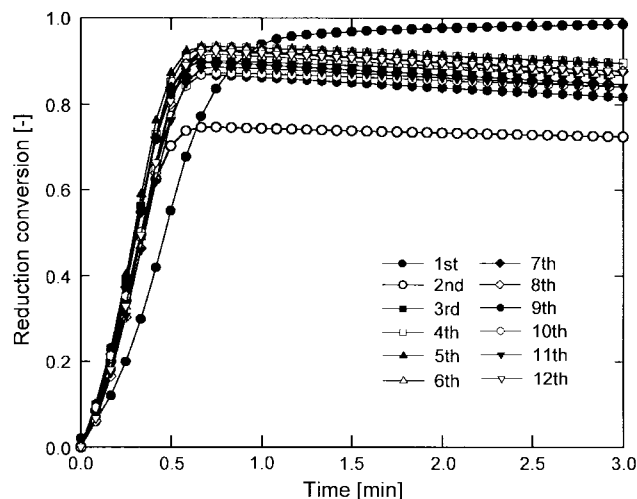


Fig. 7. Effect of cyclic reaction on reduction conversion at 900 °C.

Fig. 7 shows the cycling performance of the NiO/bentonite particles. For a few early cycles, rates of reduction were slightly changed, but they were almost the same after the third cycle. The reduction rate was apparently decreased in the second cycle, but after that, no difference was observed. For the first cycle, reduction conversion increased up to unity, but from the second cycle, reduction conversions were initially increased by reduction of metal oxides and then decreased due to carbon deposition. From the viewpoint of reduction rate, after the second cycle, slopes of the line (i.e., reduction rate) were higher than that of the first cycle and they were almost same.

Fig. 8 shows the effect of the number of cycles on carbon deposition boundary conversion. For a few early cycles, carbon deposition boundary conversions were slightly changed, but after that, no significant difference was observed. From the third cycle, carbon deposition boundary conversion maintained an average value of 0.9 (0.87-0.93). Therefore, we obtained the promising result that the NiO/bentonite particle has an excellent regenerative ability for cycling use.

Fig. 9 shows dependence of degree of carbon deposition on the

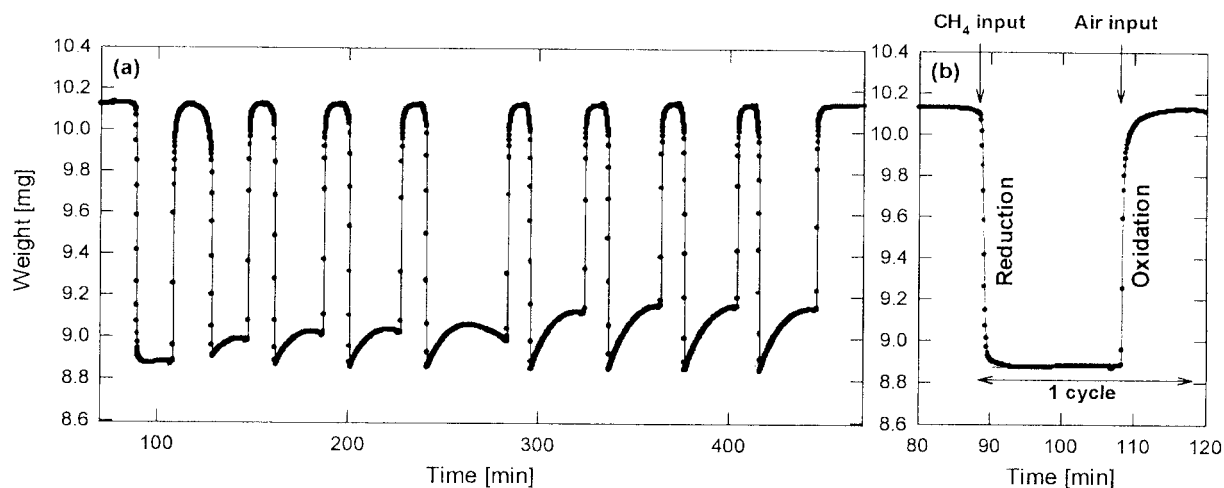


Fig. 6. Weight change of NiO/bentonite particles in cyclic reaction by CH₄ and air at 900 °C.

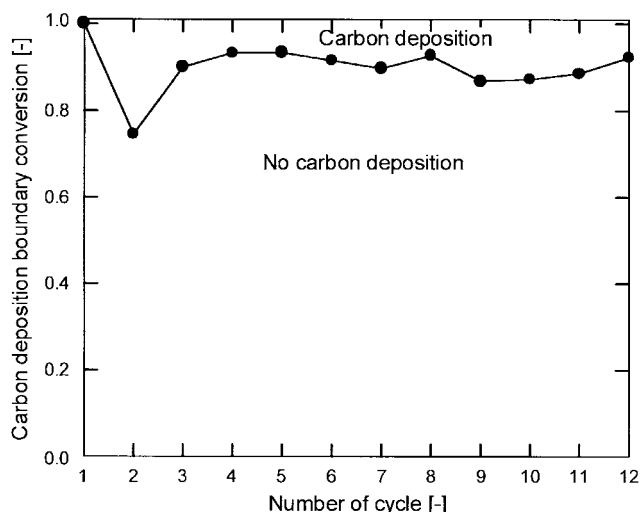


Fig. 8. Effect of cyclic reaction on carbon deposition boundary conversion at 900 °C.

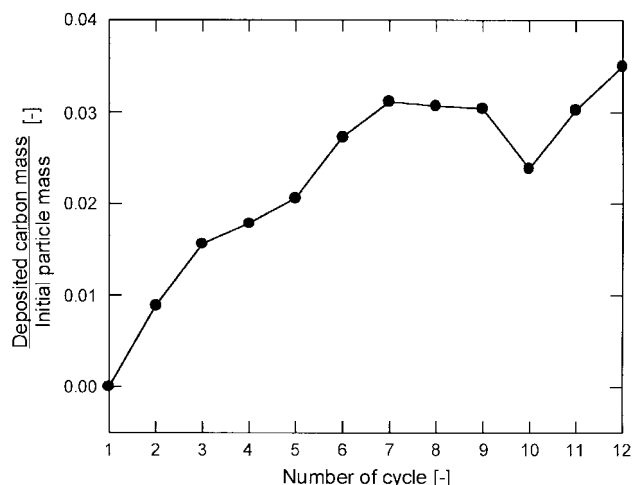


Fig. 9. Effect of cyclic reaction on degree of carbon deposition at 900 °C.

number of cycles. Degree of carbon deposition means ratio of deposited carbon weight during specific time after carbon deposition commencement to initial particle weight, and is defined as Eq. (6), where W_c is instantaneous particle weight after carbon deposition commencement, W_{min} is minimum weight (i.e., particle weight at carbon deposition boundary conversion), and W_{NiO} is completely oxidized weight (i.e., initial weight), respectively. The degree of carbon deposition increased with the number of cycles. However, after the seventh cycle, the values of degree of carbon deposition were relatively similar.

Degree of carbon deposition

$$= \frac{\text{Deposited carbon mass}}{\text{Initial particle mass}} = \frac{W_c - W_{min}}{W_{NiO}} \quad (6)$$

Fig. 10 shows dependence of reduction rate on the number of cycles. Reduction rate calculated at X was equal to 0.5. Within 12 cycles, the values of reduction rate ranged between 0.027 and 0.038 s^{-1} . These values are somewhat lower than measured values in the

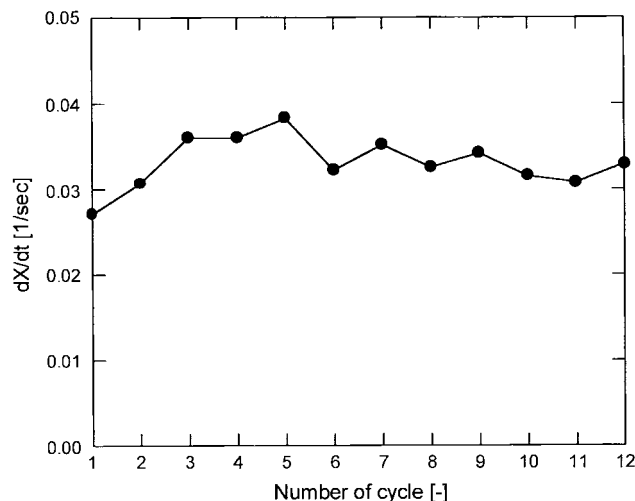


Fig. 10. Effect of cyclic reaction on reduction rate at 900 °C.

report of Ishida et al. (NiO/NiAl₂O₄ particles, 97 μm , 900 °C) [Ishida et al., 2002]. In their report, the rate of the reduction at $X=0.5$ was 0.048 s^{-1} when 100% hydrogen was fed during reduction. But, in this study, 5.04% methane was used as fuel. Assuming a first-order reaction, the reduction rate is proportional to the concentration of the reactant. Therefore, it is expected that the reduction rate of NiO/bentonite particles will be much higher than that of NiO/NiAl₂O₄ particles. As shown in the figure, the reduction rate slightly increased with the cyclic reaction to the third cycle, but after that, no significant difference was observed. It is obvious from the viewpoint of reactivity that the reduction of NiO/bentonite is fast enough to be applied in a practical system and shows good regenerative ability. Accordingly, NiO/bentonite particles not only have good reactivity but also an outstanding regenerative ability. By overcoming this crucial obstacle, we have made progress in realizing chemical looping combustion.

CONCLUSION

To develop chemical-looping combustion that may make a breakthrough in a simultaneous contribution to efficient use of energy and mitigation of greenhouse gas, we have performed experimental investigations by TGA. Reduction and carbon deposition behavior of NiO/bentonite particles depended significantly on the reaction temperature. Within the experimental range, from the viewpoints of both reduction kinetics and the resistance against carbon deposition, the appropriate temperature for NiO/bentonite particle was found to be 900 °C. Carbon deposition free map was developed and the condition that carbon deposition would be avoided was identified. Moreover, NiO/bentonite particles have good regenerative ability in both reactivity and carbon deposition. Consequently, we found that NiO/bentonite particles have excellent performance in high reactivity, avoidance of carbon deposition, and good regenerative ability. This finding supports the fact that NiO/bentonite particles are a suitable material and will play an extremely important role in the application of the chemical-looping combustion.

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NOMENCLATURE

t	: time [sec]
W	: instantaneous weight of particles [mg]
W_c	: instantaneous particle weight after carbon deposition commencement [mg]
W_{min}	: minimum weight of particle [mg]
W_{Ni}	: completely reduced weight of particles [mg]
W_{NiO}	: completely oxidized weight of particles [mg]
X	: conversion [-]

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