메탄 연소에서의 금속 산화물에 탄소 침적 및 탄화물 형성

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Carbon Deposition and Carbide Formation
on Metal Oxides in Methane Combustion

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1. Introduction

When carbohydrate fuels are burned or reformed to syngas such as CO and H_2, incomplete combustion or side reaction causes carbon deposition on metal oxides. In other gas-solid reaction such as catalytic reactions, electrochemical reactions, and hot-gas cleanup, carbon deposition on the solid metal is a fatal problem since it lowers solid reactivity and shortens its life. This carbon covers reactive sites or transforms chemical structures and consequent reduction of the reaction efficiency. To avoid carbon deposition, a high concentration of water vapor is usually needed. In the chemical-looping combustion, however, water vapor is produced as a reduction product, when hydrocarbon gas is used as a fuel [1]. Ishida et al. [2] reported that carbon was formed on oxygen carrier particles under a certain reaction condition so that the input ratio of H_2O/CO should be controlled. The carbon deposition characteristics on the metal oxides particles, NiO and Fe_2O_3, as oxygen carriers for the chemical-looping combustion have been determined in this study.

2. Theory

The mechanisms of indirect combustion of methane on NiO or Fe_2O_3 are as follows:

$$4\,NiO + CH_4 \rightarrow CO_2 + 2\,H_2O + 4\,Ni$$
$$4/3\,Fe_2O_3 + CH_4 \rightarrow CO_2 + 2\,H_2O + 8/3\,Fe$$
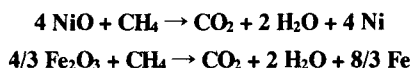
At oxygen deficiency condition, methane cracking or the Boudouard reaction may take place as:

$$CH_4 \rightarrow C + 2\,H_2$$
$$2\,CO \rightarrow C + CO_2$$
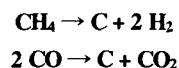
The former is the endothermic reaction, $K_p = 9.72$ at 973 K, and the latter is the exothermic reaction, $K_p = 0.96$ at 973 K. [3] By these side reactions, carbon atoms are formed and deposited on metal surface.

Sometimes they are composed with other atoms, and converted to carbide. Deposited carbon and carbide lowers activity of the particles.

3. Experiment

The NiO and Fe₂O₃ particles supported on bentonite, TiO₂, and Al₂O₃, i.e., NiO/bentonite, Fe₂O₃/ bentonite, NiO/TiO₂, Fe₂O₃/TiO₂, NiO/Al₂O₃, and Fe₂O₃/Al₂O₃ were prepared to determine the effect of supports on the reactivity. Also, the composition of NiO:Fe₂O₃ was varied to examine the effect of their loading on the reactivity. The ratios of NiO/Fe₂O₃ were 4/0, 3/1, 2/2, 1/3 and 0/4, and they were supported on bentonite. Those particles were prepared by direct mixing of fine metal oxides whose size was less than 10 μm. The ratio of carrier/support is 6/4, and the paste was made by adding distilled water to the mixed powders. The paste was dried at 383 K for 24 hours, and calcined at 1273 K for 6 hours. Then it was crushed in a ball mill, and sieved for preparing particle size range of 106~150μm. Their crystalline phases were identified by XRD from diffraction patterns between 2θ = 15° and 80° with X-ray diffractometer employing Cu Kα radiation.

In a thermobalance reactor (0.055 m-I.D, 0.60 m-height), the reactivity of the oxygen carrier particles was determined (Fig. 1) at the alternating atmosphere of oxidation and reduction reactions where an oxygen carrier particles exposing to alternating oxidation and reducing (10% CH₄, 5% CO₂, 10% H₂O) conditions at 1123 K [4] as in case of the chemical-looping combustion system.
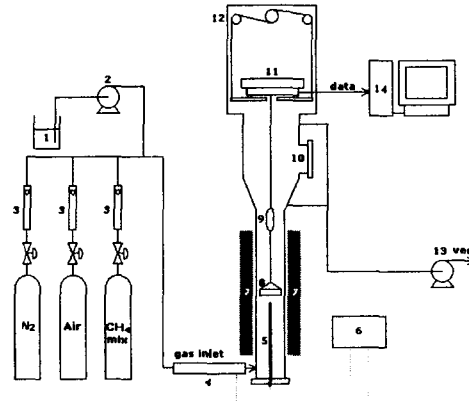

Fig. 1. Schematic diagram of thermobalance reactor

4. Result and Discussion

Composition of the metal oxide particles before and after reduction by methane is shown in Table 1. As can be seen, carbon deposition can be seen after the reduction reaction. Especially, iron oxide or bentonite, iron carbide (Fe$_x$C) or silicon carbide (SiC) are formed after reduction.

The conversion as a function of time is shown in Figures 2 and 3. Figure 2 shows the effects of supports on the conversion and Fig. 3 shows the effect of NiO and Fe₂O₃ composition on the conversion.

The conversion is defined as:

$$X = \frac{m_{ox} - m}{m_{ox} - m_{red}}$$

where m is instantaneous weight, m_{red} is the weight at fully reduced state, m_{ox} is the weight at fully oxidized state. The starting point of carbon deposition is assigned when the weight began to increase. The carbon deposition is started faster generally with more highly reactive metal oxide particles. The particles

specimen	crystalline phase	
	fresh	after reduction by methane
NiO/bentonite	NiO, NiAl$_2$O$_4$	Ni, NiAl$_2$O$_4$, SiC, C
NiO/TiO$_2$	NiO, NiTiO$_3$	Ni, NiTiO$_3$, TiO$_2$, C
NiO/Al$_2$O$_3$	NiO, Al$_2$O$_3$	Ni, Al$_2$O$_3$, C
Fe$_2$O$_3$/bentonite	Fe$_2$O$_3$, Al$_2$SiO$_5$	Fe$_2$O$_3$, SiC, Fe$_5$C$_2$, Fe$_2$C, C
Fe$_2$O$_3$/TiO$_2$	Fe$_2$O$_3$, Fe$_2$TiO$_5$	Fe$_2$O$_3$, Fe$_2$TiO$_5$, TiO$_2$, Fe$_2$C, Fe$_5$C$_2$, C
Fe$_2$O$_3$/Al$_2$O$_3$	Fe$_2$O$_3$, Al$_2$O$_3$	Fe$_2$O$_3$, Al$_2$O$_3$, Fe$_5$C$_2$, Fe$_2$C, C
NiO-Fe$_2$O$_3$/bentonite	NiFe$_2$O$_3$, NiO, Fe$_2$O$_3$	FeNi$_3$, NiFeO$_4$, Ni, Fe$_2$O$_3$, SiC, Fe$_5$C$_2$, Fe$_2$C, C

Table 1. XRD patterns of metal oxides before and after reduction by methane

supported on bentonite do not produce fast reactivity, but carbon deposition begins more slowly than the other metal oxide particles. The particles supported on Al$_2$O$_3$ exhibit fast reaction patterns, but carbon deposition begins earlier than any other particles. Especially NiO/bentonite gone to the conversion up to 0.9 without carbon deposition. For application to the chemical-looping combustion, the conversion rate of oxygen carrier particles must be controlled before carbon deposition starts.

We analysed more about NiO-Fe$_2$O$_3$/bentonite particles which have good resistance against carbon deposition. Fig. 3 shows that more NiO content yields better reactivity and higher conversion. Also, higher NiO contents lead faster carbon deposition as carbon deposition begins on NiO/bentonite from around 5,000 s, and the deposition on Fe$_2$O$_3$/bentonite starts from over 10,000 s. To apply an oxygen
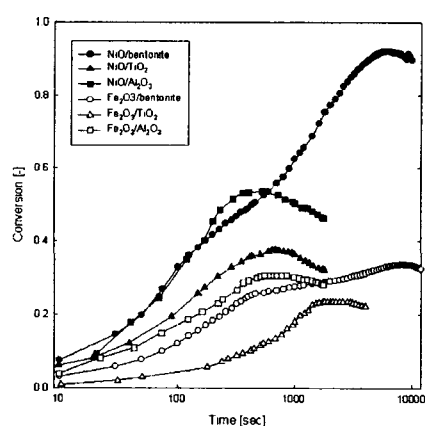

Fig. 2. Conversion change of NiO and Fe$_2$O$_3$ particles supported on bentonite, TiO$_2$, and Al$_2$O$_3$
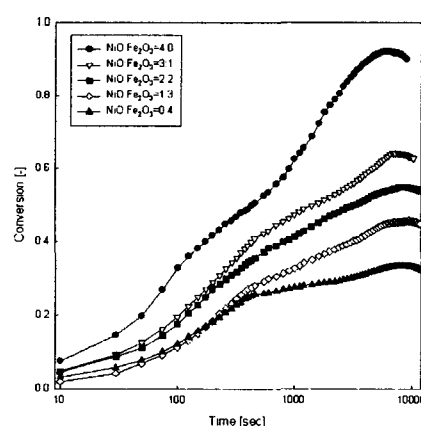
Fig. 3. Conversion change of NiO-Fe$_2$O$_3$/ bentonite particles which have different composition

carrier particles for the chemical-looping combustion process, however, fast reaction is important so that the conversion after 1,000 s does not have any meaning to the process. Therefore, NiO/bentonite is the best oxygen carrier based on the reactivity or carbon deposition.

5. Conclusion

Carbon depositions on NiO and Fe_2O_3 supported on bentonite, TiO_2, and Al_2O_3 were determined in a thermobalance reactor from the reduction reaction by methane combustion. Carbon and some carbide are formed after reduction, and the crystalline phase was found by XRD analysis. The carbon deposition starts faster with more highly reactive particles. The metal oxide particles supported on bentonite do not exhibit high reactivity, but carbon deposition began rather slowly at the conversion above 0.9 than the other metal oxide particles. More NiO content yields better reactivity and higher conversion but it leads faster carbon deposition. To apply an oxygen carrier for the chemical-looping combustion process, however, fast reaction is more important, therefore, NiO/bentonite is the best oxygen carrier based on the reactivity or carbon deposition.

6. References

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