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## Effects of reduction on the catalytic performance of limonite ore

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### ABSTRACT

The catalytic performance of Ni-containing limonite ore in the dry reforming reaction of methane ( $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{H}_2 + 2\text{CO}$ ) was determined before and after hydrogen reduction, and under a flow of hydrogen. After hydrogen reduction, the limonite ore exhibited higher catalytic performance, because of the formation of Fe–Ni. However, the Fe in Fe–Ni was readily oxidized by the input  $\text{CO}_2$  gas, resulting in a rapid decrease in the catalytic performance of limonite ore. The performance decrease was due to a decrease in the Ni surface area; Ni could not dissolve in iron oxides and this caused segregation in the iron oxides. When the reaction was conducted under a hydrogen flow, the Fe–Ni was formed and maintained. Ni was highly dispersed in the Fe–Ni phase, resulting in greater surface area of Ni and higher conversion rate of  $\text{CH}_4$  and  $\text{CO}_2$ . The catalytic performance of the limonite ore was inferior to the  $\text{Ni}/\text{Al}_2\text{O}_3$  catalyst because the effect of catalyst support was small, however, the limonite ore was more stable during catalytic use and much cheaper than the  $\text{Ni}/\text{Al}_2\text{O}_3$ .

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### 1. Introduction

Unutilized high-temperature waste heat and  $\text{CO}_2$  emissions are important issues in the steel industry. Significant amounts of high-temperature waste heat ( $>600$  °C) are emitted from blast furnaces, coke ovens, and converters without effective heat recovery [1]. The steel industry also emits large quantities of  $\text{CO}_2$ , which comprise around 15% of the total  $\text{CO}_2$  emissions of Japan [2]. The dry reforming reaction of methane ( $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{H}_2 + 2\text{CO}$ ;  $\Delta H = 247$  kJ  $\text{mol}^{-1}$  at 298 K) is an effective method to produce energy in the form of hydrogen and carbon monoxide from carbon dioxide and waste heat [3].

The dry reforming reaction proceeds in the presence of metal based catalysts. Ni-based catalysts have been found to be one of the most effective catalysts for this reaction [4–17]. Generally, Ni-based catalysts are prepared using a wet impregnation method from Ni nitrate solution with an oxide support. To improve the catalytic performance and stability of Ni-based catalysts, many studies have been performed. For example, alkali metals or alkaline earth metals have been added to the support materials to reduce the amount of carbon deposition and to improve catalytic stability [6–8]. Ni-containing oxides, such as perovskite

and spinel compounds, exhibit strong interactions between the metal and its support [9–12]. Ni-based bimetallic catalysts have been also fabricated, and they exhibit high reactivity and stability [13–17].

In the present study, Ni-containing limonite ore was examined as a catalyst for the dry reforming reaction because of its simple preparation method, naturally occurring raw materials, low cost, and low resource utilization compared with previously reported Ni-based catalysts. Limonite ore requires only a simple dehydration process before it can be used as a catalyst. It is mainly composed of  $\text{FeOOH}$ , which is readily decomposed to porous  $\text{Fe}_2\text{O}_3$  by heat treatment at 300–800 °C [18,19]. Limonite ore is naturally occurring and readily available. Therefore, it is significantly less expensive than commercially available catalysts. Generally, Ni-supported catalysts lose their catalytic activities by carbon deposition and cannot be used after deactivation, but limonite ore can be recycled into iron and nickel by reduction after catalyst deactivation.

Previously, we reported that Ni-containing limonite ore was an effective catalyst for the dry reforming reaction [20]. Ni-containing limonite ore exhibited the highest catalytic activity of the three ore-based catalysts tested in the previous study (Ni-containing limonite ore, Ni-supported iron ore, and pristine iron ore). In this study, the effects of hydrogen reduction on the structure and catalytic performance of the Ni-containing limonite ore were examined in detail.

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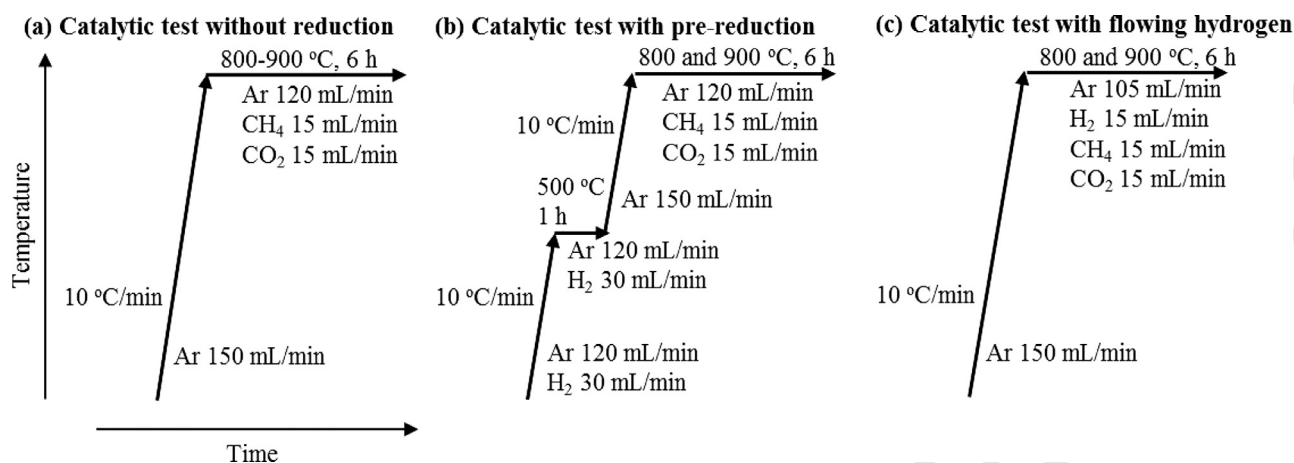


Fig. 1. Three kinds of catalytic tests conducted in this study.

## 48 2. Experimental

### 49 2.1. Preparation of catalysts from limonite ore

50 Limonite ore (from Philippines) containing 1.18 wt% Ni, 47.98  
51 wt% Fe, 0.14 wt% S, 2.12 wt% SiO<sub>2</sub>, 1.26 wt% MnO, 0.47 wt% MgO,  
52 0.10 wt% TiO<sub>2</sub>, 3.32 wt% Cr<sub>2</sub>O<sub>3</sub>, 0.10 wt% Co<sub>3</sub>O<sub>4</sub>, and 12.6 wt% of  
53 combined water (CW) was used as a catalyst for the dry reforming  
54 reaction of methane. This limonite ore was crushed into 125–  
55 300 μm sized particles and heated to 500 °C at a heating rate of  
56 5 °C min<sup>-1</sup>; subsequently, it was calcined at this temperature for  
57 4 h in air using a muffle furnace to remove any CW. These calcina-  
58 tion conditions were enough for the complete dehydration of the  
59 limonite ore [20].

60 10 wt% Ni/Al<sub>2</sub>O<sub>3</sub> catalyst as a reference was prepared by the fol-  
61 lowing steps. α-Al<sub>2</sub>O<sub>3</sub> reagent (35–50 μm, 99.0% up, Kanto Chemi-  
62 cal Co., Inc., Tokyo, Japan) was added into Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O aqueous  
63 solution and the solution was evaporated at 80 °C. The obtained  
64 material was then calcined at 500 °C for 4 h in air.

### 65 2.2. Catalytic tests

66 The apparatus for the catalytic tests in this study was same  
67 as reported in detail elsewhere [20]. The dehydrated limonite ore  
68 was placed in a packed bed reactor consisting of a quartz tube  
69 (φ6 mm × 554 mm) and an infrared gold image furnace (RHL-  
70 E410P, ADVANCE RIKO, Inc., Yokohama, Japan). The temperature of  
71 the furnace was measured using a thermocouple placed just below  
72 the catalyst and controlled with a temperature controller. The cata-  
73 lysts were placed in the quartz reactor. The amount of the limonite  
74 ore catalyst and the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst were 300 and 30 mg, respec-  
75 tively. Different amount of the catalysts was placed to set almost  
76 same Ni amount in the reactor. The length of the limonite ore cat-  
77 alyst bed was around 15 mm. In all the catalytic tests, the tempera-  
78 ture of the catalyst region was maintained at 800–900 °C for  
79 6 h. Gases were flown into the reactor from its top side, and their  
80 flow rates were controlled using mass flow controllers. The input  
81 gases, CH<sub>4</sub> (>99.9%), CO<sub>2</sub> (>99.99%), and H<sub>2</sub> (>99.99999%),  
82 were diluted with Ar (>99.999%). The total flow rate of the input  
83 gases was maintained at 30 L h<sup>-1</sup> g<sup>-1</sup> catalyst. The effects of hydrogen  
84 reduction on the catalytic performance of the limonite laterite ore  
85 were determined using three different experiments (Fig. 1).

#### 86 2.2.1. Catalytic tests without pre-reduction

87 The limonite ore catalyst was heated to 800–900 °C at a heating  
88 rate of 10 °C min<sup>-1</sup> in an Ar flow of 150 mL min<sup>-1</sup>. Just before the

target temperature was reached, Ar (120 mL min<sup>-1</sup>), CH<sub>4</sub> (15 mL  
min<sup>-1</sup>) and CO<sub>2</sub> (15 mL min<sup>-1</sup>) were flown over the catalyst. Af-  
ter that, the catalyst region was maintained at these conditions for  
6 h (Fig. 1a).

#### 2.2.2. Catalytic tests with pre-reduction

93 In this experiment, the limonite ore catalyst was reduced by hy-  
94 drogen prior to the catalytic tests. The catalyst region was heated  
95 to 500 °C at a heating rate of 10 °C min<sup>-1</sup> and maintained at  
96 500 °C for 1 h while Ar (120 mL min<sup>-1</sup>) and H<sub>2</sub> (30 mL min<sup>-1</sup>) were  
97 flown over the catalyst. After the reduction process was complete,  
98 the H<sub>2</sub> flow was stopped and the catalyst was heated to 800 or  
99 900 °C at a rate of 10 °C min<sup>-1</sup>. Just before the target tempera-  
100 ture was reached, Ar (120 mL min<sup>-1</sup>), CH<sub>4</sub> (15 mL min<sup>-1</sup>), and CO<sub>2</sub>  
101 (15 mL min<sup>-1</sup>) were flown over the catalyst. After that, the catalyst  
102 region was maintained in this condition for 6 h (Fig. 1b).  
103

#### 2.2.3. Catalytic tests with hydrogen flow

104 The limonite ore catalyst was heated to 800–900 °C at a heat-  
105 ing rate of 10 °C min<sup>-1</sup> in an Ar flow (150 mL min<sup>-1</sup>). Just before  
106 the target temperature was reached, Ar (105 mL min<sup>-1</sup>), H<sub>2</sub> (15 mL  
107 min<sup>-1</sup>), CH<sub>4</sub> (15 mL min<sup>-1</sup>), and CO<sub>2</sub> (15 mL min<sup>-1</sup>) were flown  
108 over the catalyst. After that, the catalyst region was maintained in  
109 this condition for 6 h (Fig. 1c).  
110

### 2.3. Characterization

111 In each catalytic test, the composition of the outflow gases  
112 was determined at 5 min interval using gas chromatography (Ag-  
113 ilent 3000, INFICON Co., Ltd., Yokohama, Japan). Before and after  
114 the catalytic tests, phase identification and surface observation  
115 measurements of the limonite ore were conducted using X-ray  
116 diffractometry (XRD; Miniflex, Rigaku, Tokyo, Japan) and scanning  
117 electron microscopy (SEM; JSM-7001FA, JEOL, Tokyo, Japan) with  
118 energy dispersive X-ray spectroscopy (EDS). The specific surface  
119 area of the limonite ore was evaluated by N<sub>2</sub> gas adsorption  
120 measurements (Autosorb 6AG, Yuasa Ionics CO. Ltd., Osaka, Japan).  
121 Carbon formation on the catalysts was observed using a CHN/O/S  
122 elemental analyzer (CE-440; EAI, United States).  
123

## 3. Results and discussion

### 3.1. Specific surface areas of the limonite ore catalysts

124 The specific surface areas of the limonite ore catalysts were  
125 evaluated by the Brunauer-Emmett-Teller (BET) model. Table 1  
126  
127

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