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Effect of steam and hydrogen treatments on the catalytic activity of pure Ni honeycomb for methane steam reforming

Ya Xu[a,*], Toshiko Harimoto[a], Linsheng Wang[a], Toshiyuki Hirano[a], Hirotaka Kunieda[b], Yuta Hara[b], Yasushi Miyata[c]

[a] National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki, 305-0047, Japan
[b] Hiroshima Co. Ltd., 41 Torashinden, Odaka, Midori, Nagoya, 459-8001, Japan
[c] Nagoya Municipal Industrial Research Institute, 4-41, 6-3 Atsuta, Nagoya, 456-0058, Japan

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ABSTRACT

The effect of steam and hydrogen treatments on the catalytic properties of a high-cell-density pure Ni honeycomb catalyst for methane steam reforming was investigated. A pretreatment consisting of steam treatment and subsequent hydrogen reduction at 1173 K significantly enhanced the catalytic activity of the Ni honeycomb catalyst at low temperatures below 1073 K. *In situ* X-ray absorption fine structure spectroscopy analysis showed that during the steam treatment, the surface Ni atoms were oxidized, and then these oxides were completely reduced to metallic Ni during the subsequent hydrogen reduction. The evolution analysis in surface morphology during pretreatment showed that many fine Ni particles formed on the surface. This surface structure was considered to be catalytically active for the methane steam reforming which is known to be structure sensitive.

1. Introduction

Developing high-performance and low-cost catalysts for methane steam reforming (MSR) in small-scale hydrogen production is becoming increasingly important because of the increasing use of hydrogen for automobile and household fuel cells [1–3]. Unlike MSR catalysts used for large-scale hydrogen production in industrial plants [4,5], those used in small-scale hydrogen production in fuel cells should be compact, have high heat and mass transfer ability, and bear frequent start/stop operation [3,6,7]. Metallic honeycomb catalysts have several advantages compared with conventional pelleted catalysts, such as: low pressure drop per catalyst volume, fast heat and mass transport, and high surface-to-volume ratio [8–10]. These advantages are important for their applications in on-site type hydrogen stations and small-scale hydrogen production systems. Usually, it is necessary to deposit a thin porous oxide layer with active metals on the walls of a honeycomb catalyst which leads to the requirement of expensive honeycomb catalysts [11–13]. Recently, we have developed a pure Ni honeycomb catalyst with a high cell density of 900 cpsi without using noble metals and porous oxide supports [14]. It was found that the Ni honeycomb catalyst exhibited good catalytic properties for MSR at 1073 K for more than 8000 h under low steam-to-carbon ratio (S/C = 1.34) and gas hourly space velocity (GHSV = 335 h^{-1}) conditions. These results reveal the possibility of developing a new type of honeycomb catalyst using only Ni foil without coating an active layer on the surface. However, improving the activity of the Ni honeycomb catalyst, especially at low temperatures ($<$ 1073 K), is still a challenge.

In our previous studies, we found that a pretreatment procedure consisting of steam treatment followed by hydrogen reduction effectively modified the surface structure, and enhanced the catalytic activity of Ni_3Al foils for MSR [15,16]. The enhancement in catalytic activity was attributed to the fine metallic Ni particles formed on the foil surface during pretreatment. In this study, we aimed to apply such pretreatment to a pure Ni honeycomb catalyst for enhancing its catalytic activity at low temperatures. We found that the steam treatment followed by hydrogen reduction can affect the surface microstructure of the Ni foil, forming an active surface structure consisting of Ni nanoparticles, which significantly enhanced the catalytic activity of the Ni honeycomb catalyst. Based on these results, we found out an optimized combination of steam and hydrogen reduction at appropriate temperatures to enhance the catalytic activity of Ni honeycomb catalyst.

Hydrogen reduction at 1073–1173 K can effectively regenerate the activity of Ni honeycomb catalysts when they become gradually deactivated after extended use [14][11]. It was speculated that regeneration was achieved by reducing the Ni oxides formed by oxidizing the surface Ni atoms with steam during the reaction, but only limited experimental data supporting this speculation were found. In this study, we performed an *in situ* X-ray absorption fine structure spectroscopy (XAFS)

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[*] Corresponding author.
E-mail address: xu.ya@nims.go.jp (Y. Xu).

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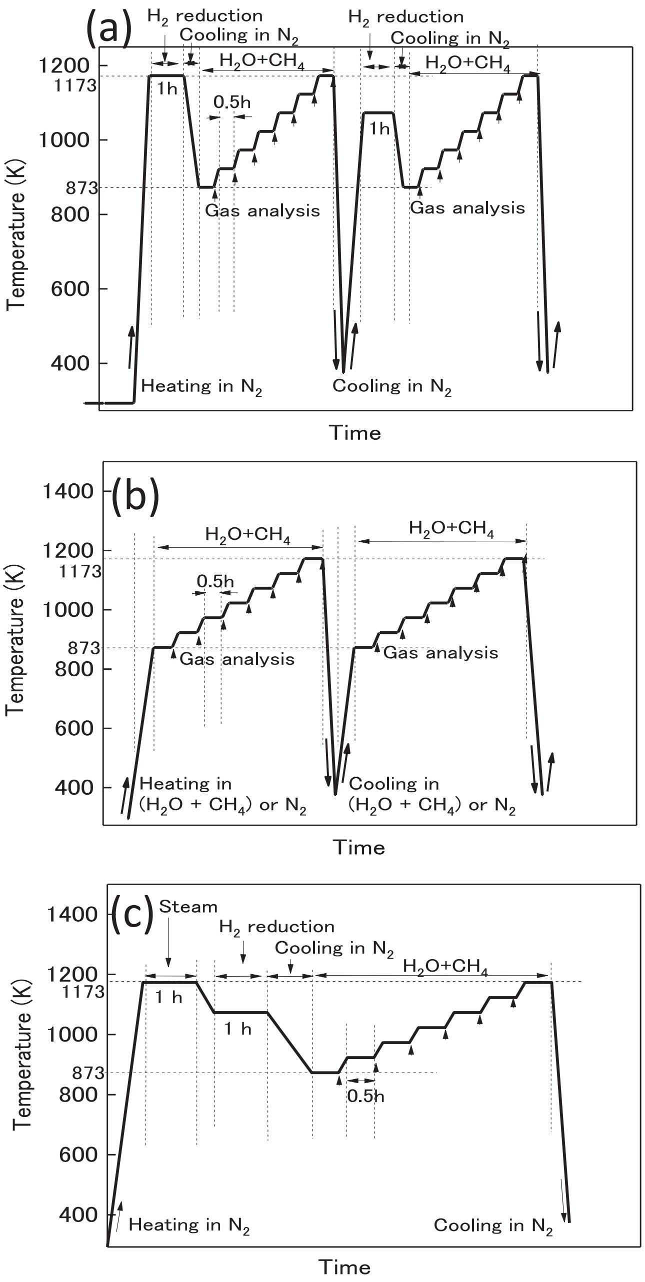

Fig. 1. Schematic representation of the isochronal tests. (a) Pattern A, the test with a H_2 pre-reduction at various temperatures; (b) Pattern B, the test without H_2 pre-reduction but changing the atmosphere (N_2 flow or reaction condition (steam + CH_4)) for cooling and heating; (c) Pattern C, the test with a steam pretreatment followed by the H_2 reduction at various temperatures.

experiment to obtain experimental evidence for the influence of the steam and hydrogen reduction treatments on the chemical states of the Ni honeycomb catalyst, and ascertain the possible reasons for the deactivation and regeneration in this catalyst. In addition, the influence of steam on the catalytic properties of Ni honeycomb during cooling and heating was examined to evaluate its catalytic performance at startup and shutdown in the presence of steam in practical applications.

2. Experimental

2.1. Ni honeycomb preparation and catalytic reaction

A honeycomb catalyst (diameter 8 mm, height 10 mm) with a cell density of 2300 cpsi was assembled by combining 30 μm thick flat and wave-shaped pure Ni foils. The details of the Ni honeycomb preparation have been described in our previous report [14].

Steam and hydrogen treatments and MSR were carried out over a single honeycomb catalyst in a conventional fixed-bed flow reactor using a quartz tube with an internal diameter of 8 mm. In order to examine the effects of hydrogen reduction and steam treatment, three test patterns were designed, as shown in Fig. 1. In Pattern A, prior to the reaction, the catalyst was first reduced at 873 K for 1 h using a flow of H_2 (30 mL(STP)/min) and N_2 (5 ml(STP)/min) (where STP stands for standard temperature and pressure: 273 K and 100 kPa). It should be noted that all the volume values from here on in are measured at STP. After the reduction, N_2 flow was introduced to flush the H_2. Subsequently, CH_4 (10 mL/min) and steam (13.6 mL/min) were introduced to the reactor with a flow of N_2 (30 mL/min). The S/C was 1.36, and the GHSV was 6400 h^{-1}. The reaction temperature was increased from 873 K to 1173 K in.50 K increments. While heating, the outlet gas composition and total flow rate were isochronally measured using an on-line gas chromatograph (GC; GL Science, GC323) and a gas flow meter, respectively, after holding each temperature stage for 30 min. After the last measurement at the highest temperature, the catalyst was furnace-cooled down to the temperatures below 373 K in a flow of N_2 and the same isochronal test was repeated by varying the hydrogen reduction temperature on four levels from 873 K to 1173 K.

In Pattern B (Fig. 1(b)), after the first test using Pattern A, the catalyst was cooled down to the temperatures below 373 K and reheated to 873 K in a flow of the feed gas (CH_4 + H_2O) or N_2. Subsequently the same isochronal test was repeated without hydrogen pre-reduction. In Pattern C, the catalyst was pretreated at 1173 K or 873 K in a flow of steam (37 mL/min) with N_2 (30 mL/min) followed by the hydrogen reduction at 1173 K or 873 K (30 mL/min) with N_2 (5 mL/min), and then single isochronal test was carried out. In this pattern, fresh catalysts were used for each test.

2.2. Catalyst characterization

The Brunauer-Emmett-Teller (BET) specific surface area of the honeycomb before and after the reactions was measured with Kr adsorption using a surface area analyzer (Micromeritics, ASAP 2020). The surface morphology was analyzed using a scanning electron microscope (SEM; JEOL, JSM-7000 F) coupled with an X-ray energy dispersive spectroscopy (EDS) system.

In situ XAFS experiments were carried out at the XAFS BL5S1 beamline of the Aichi Synchrotron Radiation Center [17,18] to examine chemical state changes during steam and hydrogen reduction. The storage ring was operated at 1.2 GeV, and the beamline was designed for measurements in the 5–20 keV energy range, with a 7000 energy resolution ($E/\Delta E$) at 12 keV. The beam spot size at the sample position equaled 0.4 × 0.14 mm^2. Flow rates of H_2 and N_2 were controlled using digital mass flow meters, and H_2O flow was controlled using a plunger pump. The above species were mixed in an evaporator heated to 423 K before being introduced into the cell. A 20 μm-thick pure Ni foil sample of diameter 10 mm was used for XAFS measurements. We recorded XAFS data in the transmission mode during the following operations. The sample was heated to 873 K in a flow of N_2, and reduced at this temperature for 1 h in a flow of H_2 (100 mL/min). Subsequently, the sample was heated to 1173 K and kept in a flow of N_2 (100 mL/min) and H_2O (26 μL/min) for 30 min. Subsequently, the H_2O feed was stopped and H_2 (100 mL/min) was introduced along with N_2 carrier gas (100 mL/min) to reduce the foil at 1173 K for 30 min. All data were analyzed using the ATHENA software [19].

3. Results and discussion

3.1. Catalytic properties of Ni honeycomb after hydrogen reduction

The isochronal tests with hydrogen reduction at different