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Catalytic Activity of Oxidation-reduction Pre-treated Ni_3Al for Methane Steam Reforming

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Abstract. The catalytic activity of oxidation-reduction pre-treated Ni_3Al powder for methane steam reforming was examined. The oxidation-reduction pre-treatment consisted of two steps: oxidation in air at various temperatures from 973 to 1373 K, and then followed by reduction in H_2 at 873 K. It was found that the oxidation-reduction treatments significantly reduced the onset temperature of activity, i.e., improved the activity of Ni_3Al powder at low temperatures. The characterization of Ni_3Al surface showed that an outer surface layer of fine NiO particles were formed on the surface of Ni_3Al after oxidation. These NiO particles were reduced to metallic Ni by the subsequent reduction treatment, resulting in the high activity for methane steam reforming. These results indicate that the Ni_3Al can form highly active surface structure with oxidation-reduction treatment, having excellent heat resistance.

Introduction

Hydrogen is attracting much attention as a clean and efficient energy source. Currently, methane steam reforming, as described below, is one of the most important technologies for the hydrogen production.

$$CH_4 + H_2O \Leftrightarrow 3H_2 + CO \quad \triangle H^0_{298\,K} = +206\ \mathrm{kJ\ mol^{-1}}. \tag{1}$$

Since the methane steam reforming reaction is highly endothermic, it requires high reaction temperature, usually higher than 1000 K, to get high conversion of CH_4 to H_2 and CO [1-3]. Ni-based catalysts are commonly used for this reaction because Ni is relatively economical and active. However, their catalytic performance is not satisfactory due to deactivation which may be caused by sintering at high temperatures [4]. It is necessary to develop efficient, low-cost and thermostable catalysts for methane steam reforming.

Ni_3Al intermetallic compound has been known as a promising high-temperature structural material because of its excellent high temperature strength and corrosion/oxidation resistance [5-8]. Recently, we found that Ni_3Al, in the form of both powder and foil, shows high catalytic activity and selectivity for methanol decomposition [9-11] and methane steam reforming [12-14], indicating a possibility to develop Ni_3Al as catalysts for hydrogen production. It was found that the catalytic properties of Ni_3Al can be significantly improved by surface treatments, such as alkali and/or acid leaching [5,12,13]. The enhancement was attributed to the formation of fine Ni particles on the surface of Ni_3Al. More recently, we found that it is possible to modify the surface structure of Ni_3Al foil simply by oxidation-reduction treatment, forming a structure of Al oxide supported fine Ni particles on Ni_3Al foil surface [15]. In the present study, we carried out such oxidation-reduction treatment for atomized N_3Al powder, and examined their catalytic performance for methane steam reforming.

Experimental

A stoichiometric Ni_3Al (Ni-25 at.% Al) powder was prepared by a gas atomizing process (Kojundo Chemical Lab. Co. Ltd., Japan). The powder with a size of 75~150 μm was sieved for the study. The oxidation was carried out at 973 K, 1173 K, and 1373 K in air for 1 hour, respectively. The oxidized powder was reduced at 873 K for 1 hour in flowing hydrogen prior to the methane steam reforming in a conventional fixed-bed flow reactor. The amount of the Ni_3Al powder for reaction was 0.4 g. The reactants of CH_4 and H_2O (molar ratio of $H_2O/CH_4 = 3$) were introduced into the reactor at the gas hourly space velocity (GCSV) of 12000 h^{-1} (defined as the volume of CH_4 passed over the unit volume of catalyst per hour). Two types of reaction tests, isochronal test and isothermal test, were carried out. The details of the reaction tests were described in the previous reports [11,12]. The surface morphology and composition of the powder were analyzed by scanning electron microscopy (SEM, JEOL, JSM-7000F) coupled with an X-ray energy dispersive spectroscopy (EDS) system. The crystal structure was analyzed by X-ray diffraction (XRD) using a Cu K_α source (Rigaku, RINT2500). The reduction behaviour of the Ni oxides was examined by temperature-programmed reduction (TPR) measurement.

Results and discussion

Catalytic activity. The catalytic activity of oxidation-reduction pre-treated powder (oxidation temperature: 973 K) was isochronally measured from 873 K to 1173 K. For comparison, the same measurement was also carried out for the as-received powder without oxidation-reduction pre-treatment. Fig.1 shows the production rate of H_2 as a function of the reaction temperature. The H_2 production rate of the pre-treated powder was above 90 ml min^{-1} g-cat^{-1} at 873 K, and showed no significant changes with the increase of reaction temperature. In contrast, the H_2 production rate of the as-received powder was nearly zero below 1123 K, and then increased markedly above 1123 K, which was consistent with our previous report [12]. These results show clearly that the oxidation-reduction pre-treatment significantly reduces the onset temperature of the catalytic

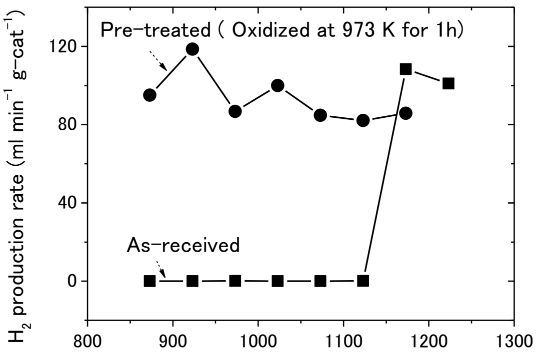

Fig. 1 H_2 production rate during methane steam reforming over oxidation-reduction pre-treated (oxidation temperature: 973 K) and as-received Ni_3Al powders as a function of reaction temperature.

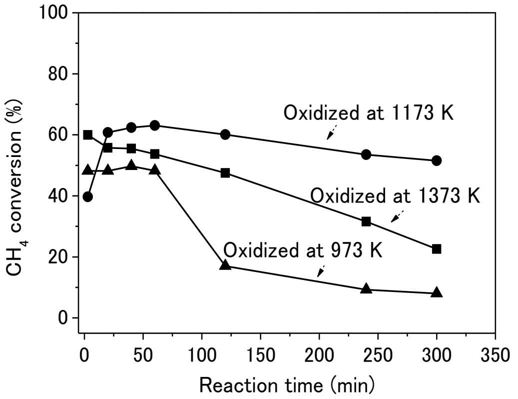

Fig. 2 Methane conversion over oxidation-reduction pre-treated Ni_3Al powders at 873 K as a function of reaction time.

activity to less than 873 K, i.e., the activity at lower temperatures is increased by the oxidation-reduction pre-treatment.

A relative small amount of CO and CO_2 were also detected as the gaseous products in addition to H_2, indicating that a side reaction, which is called water-gas shift reaction (Eq. 2), also occurred in addition to the methane steam reforming (Eq. 1).

$$CO + H_2O \Leftrightarrow H_2 + CO_2 \qquad \triangle H^0_{298} = -41 \text{ kJ mol}^{-1}. \tag{2}$$

The effect of the pre-oxidation temperature on the activity was examined by isothermal test at 873 K. Fig. 2 shows the methane conversion as a function of reaction time for the powders oxidized at 973 K, 1173 K and 1373 K, respectively. A CH_4 conversion of 40~60% was detected during the first 60 minutes of the reaction for all powders. However, the CH_4 conversion showed strong dependence on the pre-oxidation temperature with the further increase of the time, that is, it significantly decreased for the powder pre-oxidized at 973 K, but only sightly decreased for the powder pre-oxidized at 1173 K. These results indicate that the catalytic activity was significantly

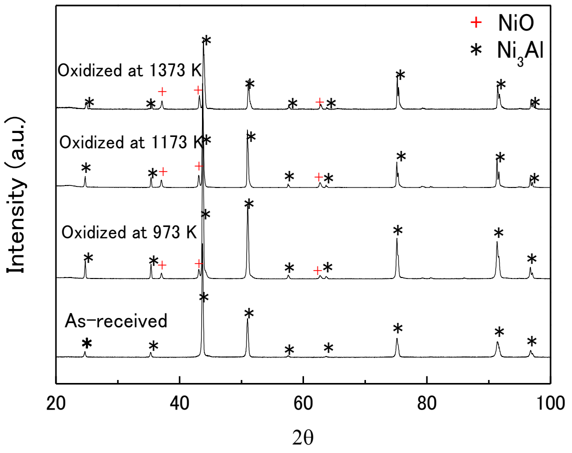

Fig. 3 XRD patterns for the as-received Ni_3Al powder and the powders pre-oxidized at 973 K, 1173 K and 1373 K for 1 h., respectively.

affected by the pre-oxidation temperature. In order to understand the effect of the pre-oxidation temperature, the surface morphology and structure before and after oxidation were analyzed as below.

XRD analysis. Fig. 3 shows the XRD patterns of the as-received powder and the powders after oxidation at 973 K, 1173 K, and 1373 K, respectively. Only Ni_3Al was identified for the as-received powder. After oxidation at each temperature, NiO was confirmed in addition to Ni_3Al, indicating the formation of NiO by the oxidation treatment. However, no obvious difference was detected from the XRD patterns among the powders oxidized at these three temperatures.

Surface morphology. Fig. 4 shows the surface morphologies of the as-received powder and the powders oxidized at 973 K, 1173 K, and 1373 K, respectively. The as-received powder showed a rapidly solidified structure by the atomizing process (Fig. 4a), as we confirmed previously [12,13]. After oxidation at 973 K, an outer layer consisted of agglomerated granular particles was formed (Fig. 4b). The EDS analysis showed this layer only contained Ni and O, corresponding to NiO. In contrast, the NiO particles changed to a fine faceted shape after oxidation at 1173 K (Fig. 4c). Furthermore, the size of these faceted particles significantly increased after oxidation at 1373 K (Fig. 4d).

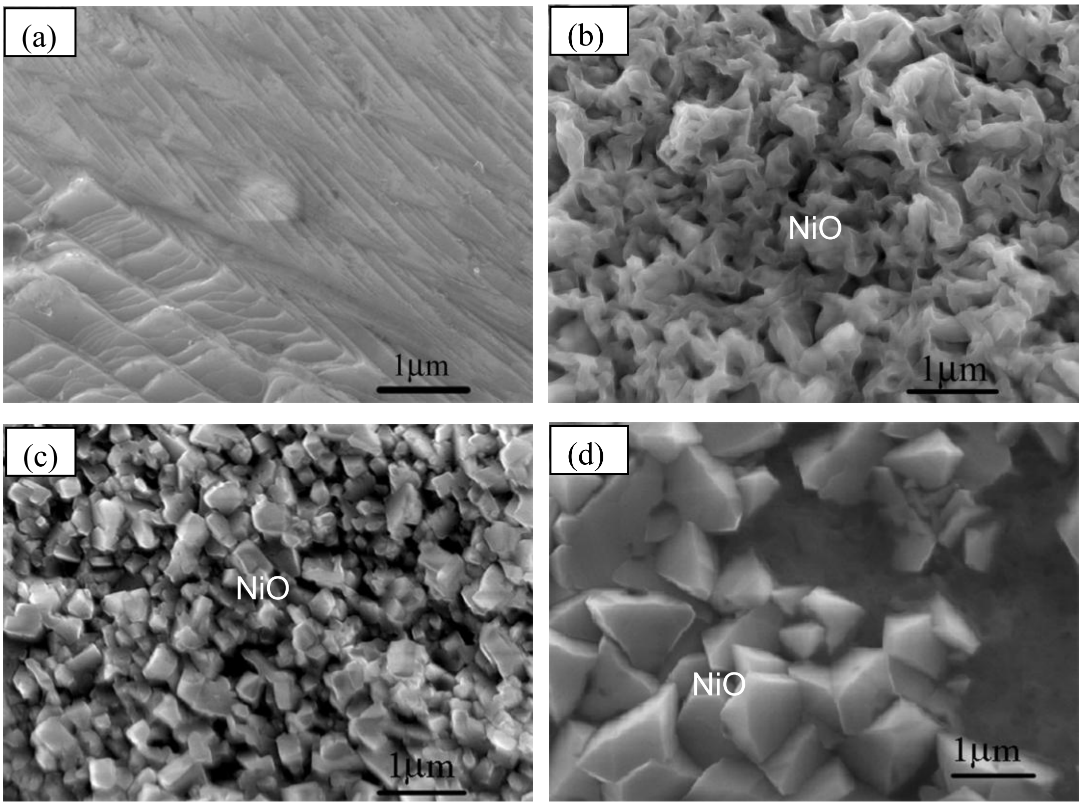

Fig. 4 Surface SEM images of the as-received Ni_3Al powder (a) and the powders after pre-oxidized at 973 K (b), 1173 K (c), and 1373 K (d) for 1h, respectively.

TPR analysis. The TPR profiles of the powders before and after oxidation are shown in Fig. 5. The TPR profile before oxidation showed a very weak peak at 473~600 K, which may corresponds to the reduction of the adsorbed oxygen-containing species [16]. After oxidation at 973 K, a strong peak appeared around 673 K, associated with two weak peaks around 773 K and 850 K. After oxidation at 1173 K and 1373 K, the strong peak shifted to the higher temperatures around 773 K, and a second peak around 850 K was also observed especially after oxidation at 1173 K. All these peaks are considered to correspond to the reduction of NiO to metallic Ni [17,18]. The difference of these peak temperatures was probably due to the difference of morphologies of the NiO after oxidation at different temperatures, as observed by SEM. It is noted that all these peak temperatures are lower than 873 K, the temperature of reduction treatment prior to reaction, indicating that the NiO particles were reduced to metallic Ni particles by the reduction treatment before the reaction. The high activity was attributed to these metallic Ni particles formed by the oxidation-reduction pre-treatment.

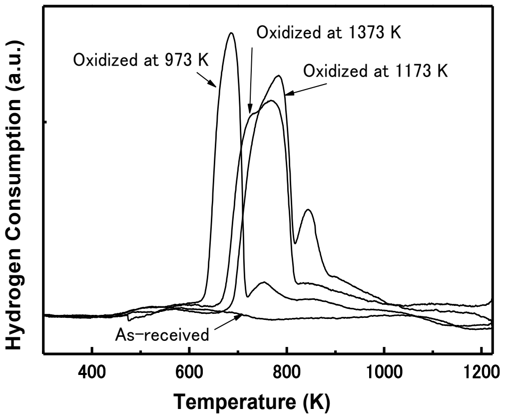

Fig. 5 TPR profiles of the as-received, and the pre-oxidized Ni_3Al powders. The measurement was carried out in a 5% H_2/Ar gas flow (20 ml min^{-1}) from room temperature to 1223 K at a heating rate of 10 K min^{-1}.

Conclusions

The effect of oxidation-reduction pre-treatment on the catalytic activity of the atomized Ni_3Al powder for methane steam reforming was examined. The following results were obtained.

1. The oxidation-reduction pre-treatment was effective for reducing the onset temperature of the activity for methane steam reforming, that is, enhancing the catalytic activity of Ni_3Al at temperature below 973 K.
2. The temperature of the pre-oxidation significantly affected the activity enhancement. The powder oxidized at 1173 K showed the best catalytic behaviour among the three kinds of powders oxidized at 973 K, 1173 K and 1373 K.
3. The characterization of Ni_3Al surface showed that fine Ni particles were formed on the surface of Ni_3Al by the oxidation-reduction pre-treatment. These fine Ni particles were considered to contribute to the enhancement of activity for methane steam reforming.

Acknowledgements

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