Ni_3Al foil as a catalyst precursor for methanol decomposition

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Efficient and low-cost hydrogen production from alcohols or hydrocarbons is a very important part of fuel cell technologies [1]. Microreactors are highly promising for this process because of high surface to volume ratio and high rates of mass and heat transfer compared with conventional reactors [2]. Generally, the micro-reactors are fabricated by the following procedures. At first, high-surface-area supports, e.g., alumina or silicon oxides are coated on the micro-channeled foils. After that, catalyst materials are coated on the supports by chemical processes such as impregnation or precipitation. Finally, reduction treatment is performed before catalytic reaction after repeating the catalyst coating process for several times [3]. As shown in the process above, one micro-reactor is made from three different materials at least, and furthermore the complex coating process of the catalysts has limited the practical application of the micro-reactors.

Recently, we found high catalytic activity and selectivity for methanol decomposition ($CH_3OH \rightarrow 2H_2 + CO$) from intermetallic compound Ni_3Al after alkali-leaching treatment [4]. Ni_3Al is known to be an excellent high-temperature structural material [5]. Its brittleness at ambient conditions, as with many other intermetallic compounds, used to be a serious problem. We have overcome this problem by directional solidification [6] and have succeeded in cold-rolling this compound into thin foils 23 μm in thickness [7]. Also, we have found that cold-rolled Ni_3Al foils possess good mechanical properties and workability [8]. Furthermore, microchannel devices have been successively fabricated using the cold-rolled foils with laser ablation and diffusion techniques [9]. This demonstrated the possibility of creating Ni_3Al-made microreactors. However, detailed study for the catalytic properties of the Ni_3Al foils has not been established, yet.

In this study, we preformed the methanol decomposition over the Ni_3Al thin foils in the temperature range of 513-793 K. Catalytic activity and stability over the Ni_3Al foils were investigated. Furthermore, the origin of enhanced catalytic activity and the process of activation were discussed.

Ni_3Al foils that were 30 μm thick (Ni-24 at.% Al) were fabricated using 98% cold rolling of single crystalline Ni_3Al ingots. Catalytic experiments were carried out over the cold-rolled foil samples in a conventional fixed-bed flow reactor made of quartz tube. These experiments were conducted in the same way described in the previous report [5]. Prior to measurement, the samples were reduced at 513 K for 3.6 ks in flowing hydrogen. After flushing the hydrogen with nitrogen, we introduced methanol to the quartz tube at a liquid hourly space velocity of 0.0011 $m^3 \cdot hr^{-1} \cdot m^{-2}$ (defined as the volume of methanol passed over the unit surface area of the foil sample per hour). The catalytic properties of the foil samples were evaluated in the temperature range of 513-793 K by analyzing the outlet composition of gaseous products with a gas chromatograph.

The surface morphologies were observed by means of scanning electron microscopy (SEM; JEOL, JSM-7000F) with a field emission gun and with transmission electron microscopy (TEM; Philips, CM 200). The crystal structure of the solid phase surface products was analyzed by means of X-Ray diffraction (XRD; Rigaku, RINT 2500V) using a Cu-Kα source. The surface area of the Ni_3Al foils was determined by Brunauer-Emmett-Teller (BET) surface area analysis. The electron binding energies of oxygen, aluminum, and nickel in the Ni_3Al foils were measured by X-ray photoelectron spectroscopy (XPS; VG Scientific, ESCALab 200R), using twin anode Al-Kα X-ray source (1486.6 eV; 250 W) and hemispherical energy analyzer.

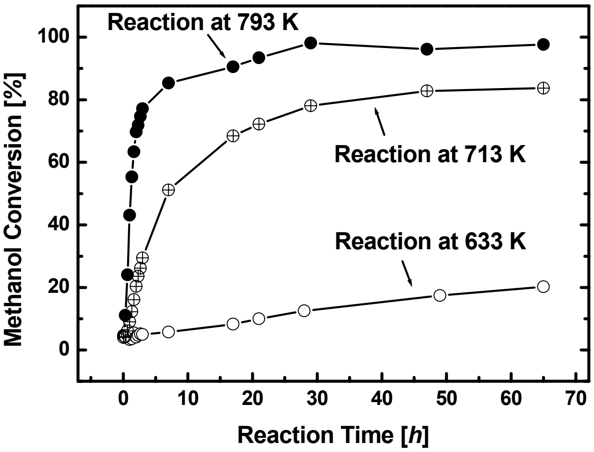

Figure 1. Methanol conversion over Ni_3Al foils as a function of reaction time at 633-793 K.

Figure 1 shows methanol conversion as a function of reaction time in the temperature range of 633-793 K. The Ni_3Al foils showed low catalytic activity initially, however, the activity increased with the increase of reaction time. In particular, above the temperatures of 713 K, the activity rapidly increased and then stabilized at high values, displaying an excellent catalytic stability. These results mean that the cold-rolled Ni_3Al foils are spontaneously activated during the reaction above 713 K.

Figure 2 shows surface structure of the Ni_3Al foils at different period of reaction time at 793 K. Before reaction, the Ni_3Al foils showed macroscopically smooth surface structure (Fig. 2a). However, drastically different surface structure was observed during the reaction. After 1 h of reaction, small particles formed on the surface of the foils (Fig. 2b). After 2 h of reaction, carbon fibers formed from the fine particles, and subsequently the density of fibers increased with increasing reaction time as shown in Figs. 2c and 2d. As a result of the carbon nanofiber formation, surface area of the foils increased to about 54 times as large as the starting value after 7 h of reaction; the surface area of the foils before and after reaction was 0.15 and 15.47 m^2/g, respectively.

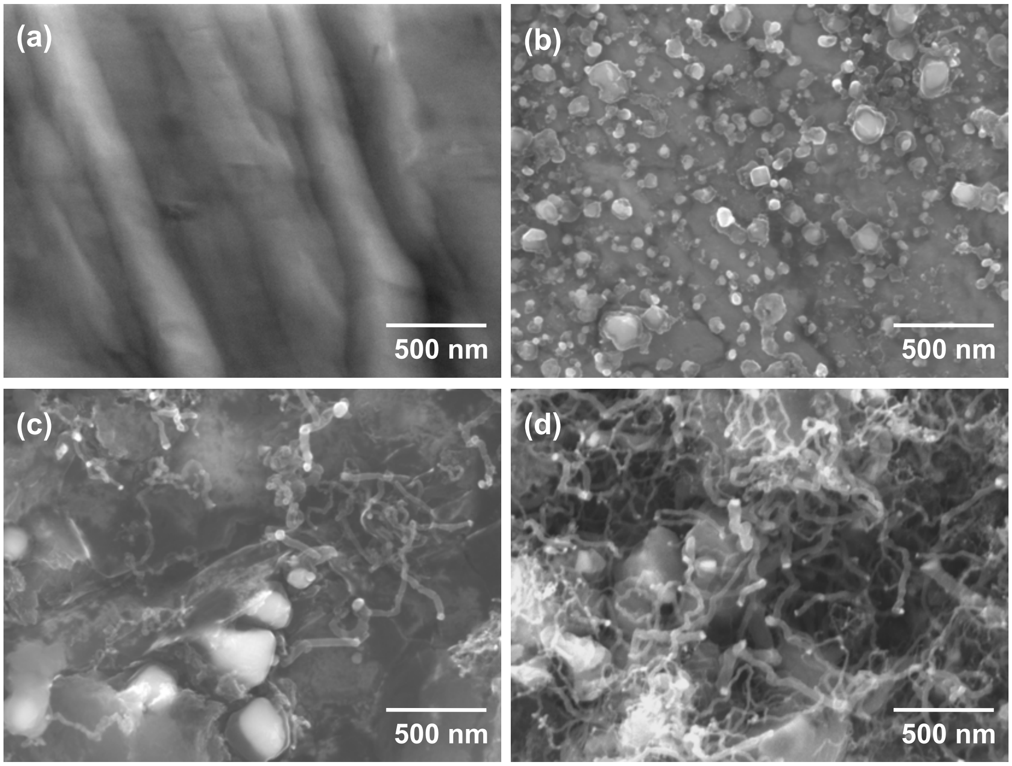

Figure 2. SEM image of Ni_3Al foils (a) before reaction and after (b) 1, (c) 2, and (d) 7 h of reaction.

The surface products were characterized by XRD and TEM after reaction at 793 K for 7 h (Fig. 3). The XRD patterns in Fig. 3a clearly showed the characteristic of graphite and Ni [10], suggesting that the fine particles in Fig. 2 corresponds to metallic Ni. From the

TEM result (Fig. 3b), it was observed that most of the fine Ni particles were dispersed on the top of carbon nanofibers. This morphology is known to be advantageous for the performance of heterogeneous catalysts. Currently, carbon nanofibers are widely used as effective catalyst supports to generate high surface area for catalytic reactions [10,11]. Therefore, the formation of this nanoscale structure is considered to contribute to the rapid increase of methanol conversion during the reaction at 793 K.

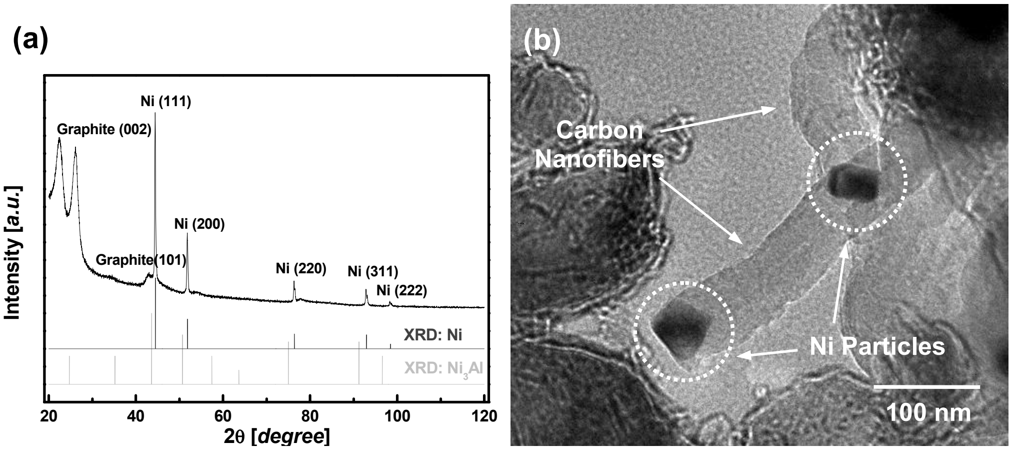

Fig. 3. (a) XRD patterns and (b) TEM result for surface products on Ni_3Al foils after 7 h of reaction at 793 K.

In order to understand the formation mechanism of the surface products, i.e., fine Ni particles and carbon nanofibers, XPS investigation was performed (Fig. 4). Before reaction, the Al2*p* spectrum showed two peaks corresponding to the binding energies of metallic Al (Al^{met}) and Al oxide (AlO_x). The AlO_x is reported to be amorphous Al native oxide on Ni_3Al alloys. The Ni3*p* spectrum showed a peak of metallic Ni (N^{met}) and/or native Ni oxide (NiO_x). The corresponding O1*s* spectra (Fig. 4b) can be well fitted by two components at binding energies of 531.2 and 532.2 eV, which correspond to the binding energies of NiO_x and AlO_x, respectively [12]. After 1 h of reaction, the Al^{met} and AlO_x peaks disappeared and were replaced by a peak at higher binding energies corresponding to those of Al_2O_3 and/or $Al(OH)_3$. The corresponding O1*s* spectra can be well fitted by two binding energies of Al_2O_3 and $Al(OH)_3$ [13]. In contrast Ni oxide was not detected. These results clearly show that Al in the Ni_3Al foils is selectively oxidized and hydroxylated to form Al_2O_3 and $Al(OH)_3$. When Al is selectively oxidized and hyroxylated, Ni atoms are left behind and aggregate into fine particles [14] as shown in Fig. 2.

We suggest that the fine Ni particles serve as catalyst for two reactions in the present study. First, they accelerate the methanol decomposition, leading to the increase of methanol conversion. At the same time, they accelerate the carbon precipitation, leading to the formation of carbon nanofibers.

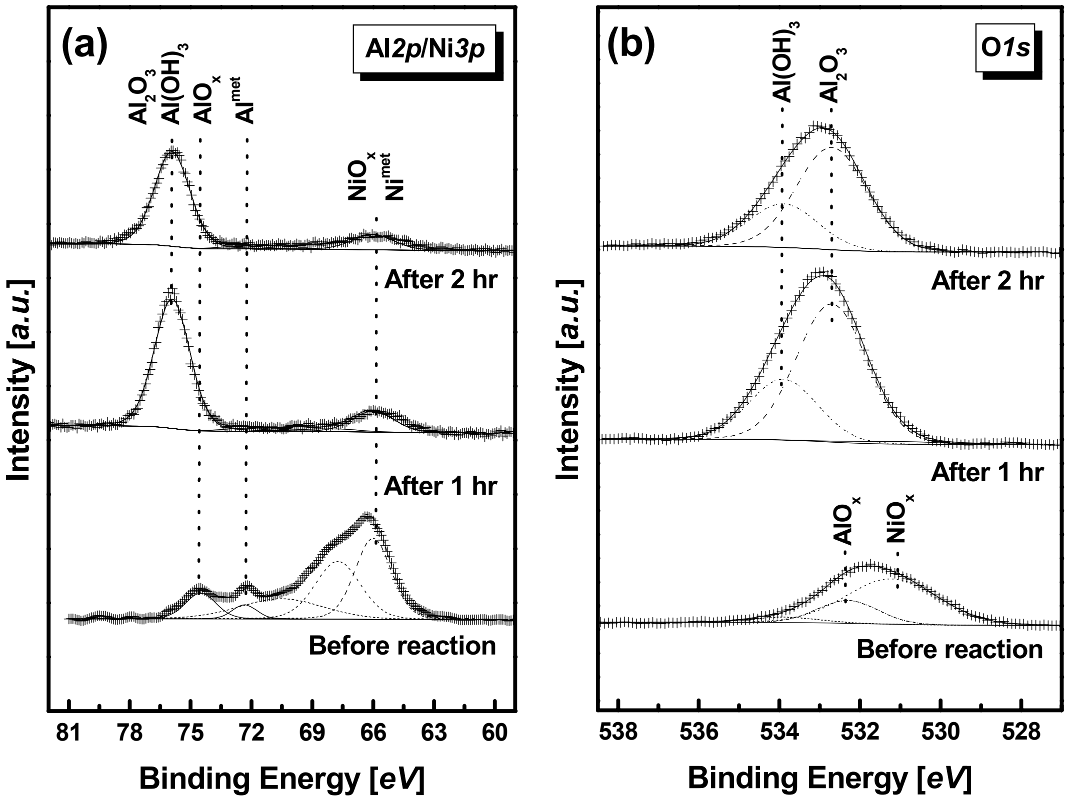

Fig. 4. XPS spectra obtained over Ni_3Al foils at different period of reaction time at 793 K. (a) Al2*p*/Ni3*p* spectra before reaction and after 1, 2, 7 h of reaction (b) O1*s* spectra after 1 and 2 h of reaction.

In conclusion, Ni_3Al foils can serve as catalyst precursors for methanol decomposition by spontaneous formation of small Ni particles supported on carbon nanofibers on their surface during the reaction. Also, they can serve as structural materials of microreactors as previously demonstrated [9]. These results show that a considerable part of microreactors for hydrogen production can be fabricated from Ni_3Al foils alone.

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Acknowledgement

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