Ni$_3$Al 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$_3$OH $\rightarrow$ 2H$_2$ + CO) from intermetallic compound Ni$_3$Al after alkali-leaching treatment [4]. Ni$_3$Al 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 $\mu$m in thickness [7]. Also, we have found that cold-rolled Ni$_3$Al 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$_3$Al-made microreactors. However, detailed study for the catalytic properties of the Ni$_3$Al foils has not been established, yet.
In this study, we performed the methanol decomposition over the Ni$_3$Al thin foils in the temperature range of 513-793 K. Catalytic activity and stability over the Ni$_3$Al foils were investigated. Furthermore, the origin of enhanced catalytic activity and the process of activation were discussed.

Ni$_3$Al foils that were 30 μm thick (Ni-24 at.% Al) were fabricated using 98% cold rolling of single crystalline Ni$_3$Al 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$^3$·hr$^{-1}$·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-K$\alpha$ source. The surface area of the Ni$_3$Al foils was determined by Brunauer-Emmett-Teller (BET) surface area analysis. The electron binding energies of oxygen, aluminum, and nickel in the Ni$_3$Al foils were measured by X-ray photoelectron spectroscopy (XPS; VG Scientific, ESCALab 200R), using twin anode Al-K$\alpha$ X-ray source (1486.6 eV; 250 W) and hemispherical energy analyzer.

![Figure 1. Methanol conversion over Ni$_3$Al foils as a function of reaction time at 633-793 K.](image-url)
Figure 1 shows methanol conversion as a function of reaction time in the temperature range of 633-793 K. The Ni$_3$Al 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$_3$Al foils are spontaneously activated during the reaction above 713 K.

Figure 2 shows surface structure of the Ni$_3$Al foils at different period of reaction time at 793 K. Before reaction, the Ni$_3$Al 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.

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 Ni3Al foils after 7 h of reaction at 793 K.](image)

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 Al2p spectrum showed two peaks corresponding to the binding energies of metallic Al (Al^met) and Al oxide (AlOx). The AlOx is reported to be amorphous Al native oxide on Ni3Al alloys. The Ni3p spectrum showed a peak of metallic Ni (Nimet) and/or native Ni oxide (NiOx). The corresponding O1s 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 NiOx and AlOx, respectively [12]. After 1 h of reaction, the Al^met and AlOx peaks disappeared and were replaced by a peak at higher binding energies corresponding to those of Al2O3 and/or Al(OH)3. The corresponding O1s spectra can be well fitted by two binding energies of Al2O3 and Al(OH)3 [13]. In contrast Ni oxide was not detected. These results clearly show that Al in the Ni3Al foils is selectively oxidized and hydroxylated to form Al2O3 and Al(OH)3. When Al is selectively oxidized and hydroxylated, 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$_3$Al foils at different period of reaction time at 793 K. (a) Al2p/Ni3p spectra before reaction and after 1, 2, 7 h of reaction (b) O1s spectra after 1 and 2 h of reaction.

In conclusion, Ni$_3$Al 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$_3$Al foils alone.

References
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