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Catalytic properties of Ni_3Al foils for methanol decomposition

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Hydrogen was produced by methanol decomposition over cold-rolled foils of intermetallic compound Ni_3Al which is known as an excellent high-temperature structural material. We found high catalytic activity and selectivity for methanol decomposition in flat cold-rolled Ni_3Al foils. The catalytic activity was enhanced above 713 K by the spontaneous formation of fine Ni particles dispersed on carbon nanofibers during the reaction, resulting in high catalytic performance. The results demonstrate that the Ni_3Al foils can be used both as catalyst precursors and as structural materials of microreactors for hydrogen production.

KEY WORDS: intermetallic compounds and alloys; fuel cell; microreactor; hydrogen production; methanol decomposition; carbon nanofibers.

1. Introduction

Efficient and low-cost hydrogen production from alcohol or hydrocarbon is an important part of fuel cell technologies [1–4]. A microreactor is a promising device for this process because of a high surface-to-volume ratio and high rates of heat and mass transfer compared with conventional reactors [5,6]. One of the key issues is to develop efficient and inexpensive heterogeneous catalysts. The catalysts are usually coated on micro-channel-structured metal sheets in the microreactors by a complex process [7–9].

Ni_3Al is known as a high-temperature structural material because of its excellent high-temperature strength and oxidation/corrosion resistance [10]. 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 [11,12] and have succeeded in cold-rolling this compound into thin foils 23 μm in thickness [13]. Recently, we also found that intermetallic compound Ni_3Al powder showed high catalytic activity and selectivity for methanol decomposition ($CH_3OH \rightarrow 2H_2 + CO$) after alkali-leaching treatment [14,15]. These results suggest a possibility of the Ni_3Al foils to be used both as catalysts and as structural sheets in the microreactors. However, the catalytic properties of the Ni_3Al have not been investigated in a form of foils. It is quite unusual to expect high catalytic performance from flat cold-rolled metallic foils because of their low surface area.

In the present study, we performed the methanol decomposition over cold-rolled thin Ni_3Al foils to study catalytic activity, selectivity, and stability in the temperature range of 513–793 K. The origin of enhanced catalytic properties and the process of activation were considered.

2. Experimental

Ni_3Al foils that were 30 μm thick (Ni-24 at.% Al) were fabricated using 98% cold rolling of single crystals without intermediate annealing [13,16]. Catalytic experiments were carried out on 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 previous reports [14,15]. 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 $0.0011\ m^3\ h^{-1}\ m^{-2}$ (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 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

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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.

3. Results and discussion

3.1. Catalytic properties

On contact with the foil samples, methanol was decomposed mainly into H_2 and CO above 713 K, and the decomposition rate increased as the temperature increased. Therefore, we focused on the catalytic properties at the highest reaction temperature of this study, 793 K. Figure 1 shows the methanol conversion and the H_2, CO, CH_4, and CO_2 selectivities as a function of the reaction time at 793 K. While it was low at the beginning, the methanol conversion rapidly increased as the reaction time increased within the first few hours, and it reached a steady state of 98% after 29 h without showing a considerable change thereafter. During the steady state, the H_2 production rate amounted to about 18,000 ml min^{-1} for the unit geometrical surface area of the foil. The H_2 and CO selectivities were almost 100% at the beginning of the reaction except before it became stable, indicating that methanol mainly decomposes into H_2 and CO, i.e., $CH_3OH \rightarrow 2H_2 + CO$. Subsequently, they slightly decreased as the reaction time increased because a small amount of CH_4, CO_2, and H_2O were produced – possibly through a water-gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) and methanation ($3H_2 + CO \rightarrow CH_4 + H_2O$) [14,15]. However, they still maintained a value greater than 80% even after 65 h. These results indicate that the cold-rolled Ni_3Al foils spontaneously changed into a material with high catalytic activity and selectivity for methanol decomposition during the reaction.

3.2. Surface characterization

A surface observation by SEM in figure 2 revealed a drastic evolution of reaction products corresponding to the change in the methanol conversion. The surface of the foil before the reaction (as-cold-rolled) was macroscopically smooth, having a rolling deformation microstructure vertical to the rolling direction [17]. After 1 h of reaction, small Ni particles (<250 nm in diameter), which were identified by XRD and back-scattered electron microscopy, formed on the surface (figure 2b). After 2 h, carbon fibers, which were also identified by XRD [18,19] (figure 3a), formed from the Ni particles. Subsequently, the density increased as the reaction time increased, as shown in figures 2c and d. A transmission electron micrograph in figure 3b shows that most of the small Ni particles are dispersed on the top of carbon nanofibers. These Ni particles supported on carbon nanofibers are known to be advantageous for the performance of heterogeneous catalysts [18–20].

The surface area of the foil samples was measured using a BET analysis. The surface area before the reaction was 0.15 m^2 g^{-1}, which was about 17 times higher than the geometrical surface area (0.00904 m^2 g^{-1}) because of the deformation structure (figure 2a). It increased to 8.02 m^2 g^{-1} after 7 h and 15.47 m^2 g^{-1} after 65 h at 793 K. These were about 54 and 104 times as large as the starting value, respectively. This sharp increase in the surface area is obviously due to the fine Ni particles and the carbon nanofibers forming, which

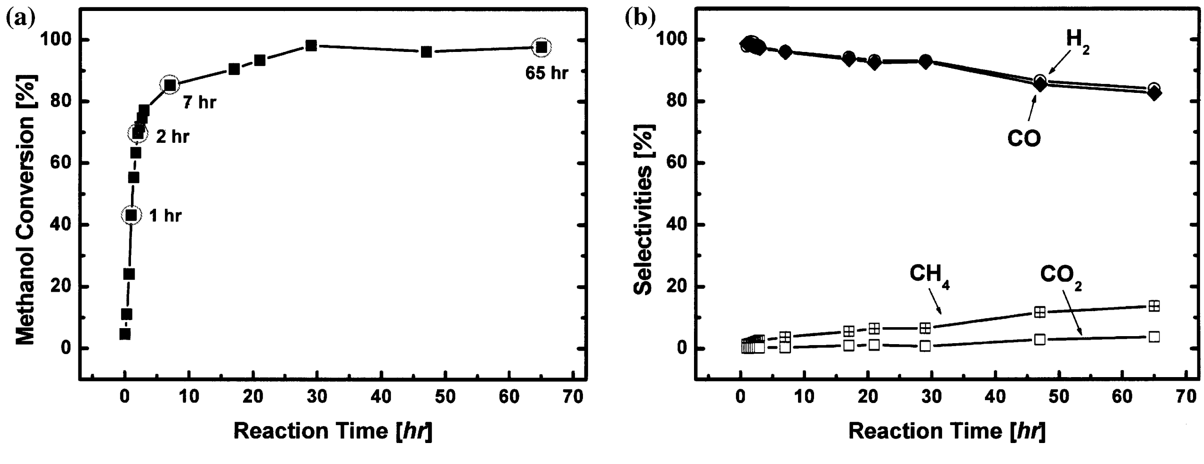

Figure 1. Catalytic properties over Ni_3Al foils for methanol decomposition. (a) Methanol conversion over Ni_3Al foils as a function of reaction time at 793 K. (b) H_2, CO, CH_4, and CO_2 selectivities over Ni_3Al foils as a function of reaction time at 793 K. *H_2 selectivity (%) = (molecules H_2 produced/C atoms in gas phase) (1/RR)×100, where RR is the H_2/CO reforming ratio; RR value for methanol decomposition is 2. **CO, CH_4, or CO_2 selectivity (%) = (C atoms in CO, CH_4, or CO_2/total C atoms in gas phase product)×100.

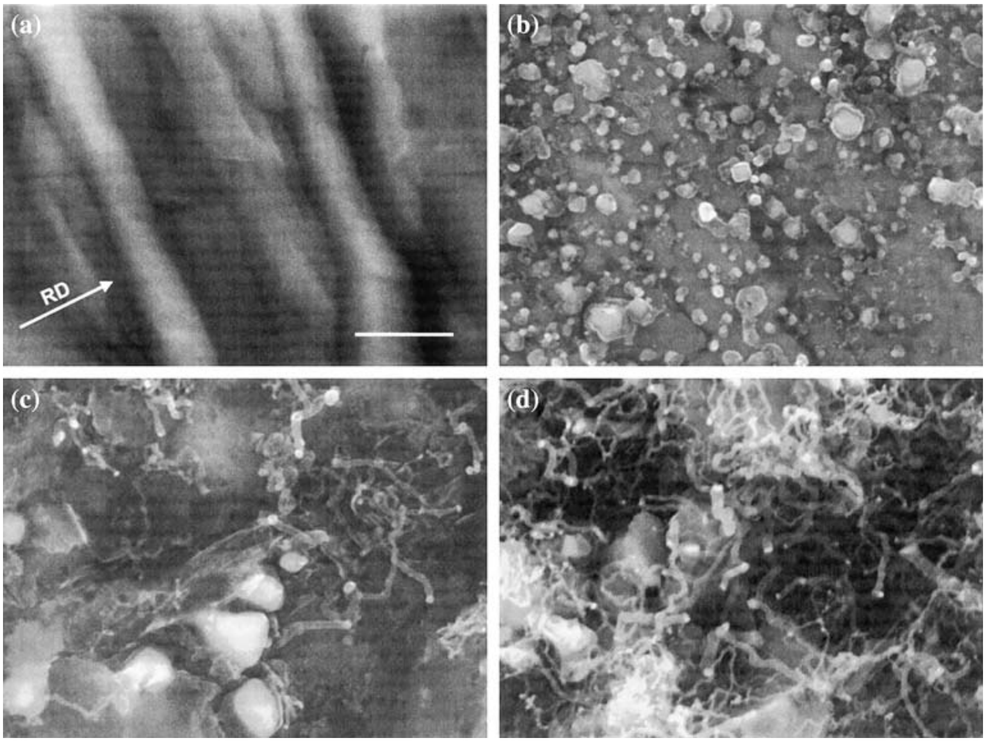

Figure 2. Structural change in Ni_3Al foils during reaction at 793 K. (a) SEM image of as cold rolled Ni_3Al foils. (b) SEM image of Ni_3Al foils after 1 h of reaction. (c) SEM image of Ni_3Al foils after 2 h of reaction. (d) SEM image of Ni_3Al foils after 7 h of reaction. The scale bar represents 500 nm. The arrow in figure 2a shows the rolling direction (RD).

contributes to the rapid increase in methanol conversion in the first few hours of the reaction shown in figure 1.

3.3. *Process of activation*

To understand the formation mechanism of the surface products, we performed an XPS investigation as shown in figure 4. Before the reaction, the Al 2*p* spectrum showed two peaks at 72.4 and 74.5 eV corresponding to the binding energies of metallic Al (Al^{met}) and Al oxide (AlO_x), respectively. This indicates the existence of native oxide before the reaction; the AlO_x is amorphous according to previous studies [21]. The Ni 3*p* spectrum showed a peak of metallic Ni (Ni^{met}) only. Native Ni oxide may form, but probably it is too thin to be detected. After 1 h, 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 O 1*s* spectra (figure 4b) can be well fitted by two components at binding energies of 532.7 and 533.9 eV, which correspond to the binding energies of Al_2O_3 and $Al(OH)_3$, respectively [22]. In contrast, Ni oxide was not detected. The results clearly

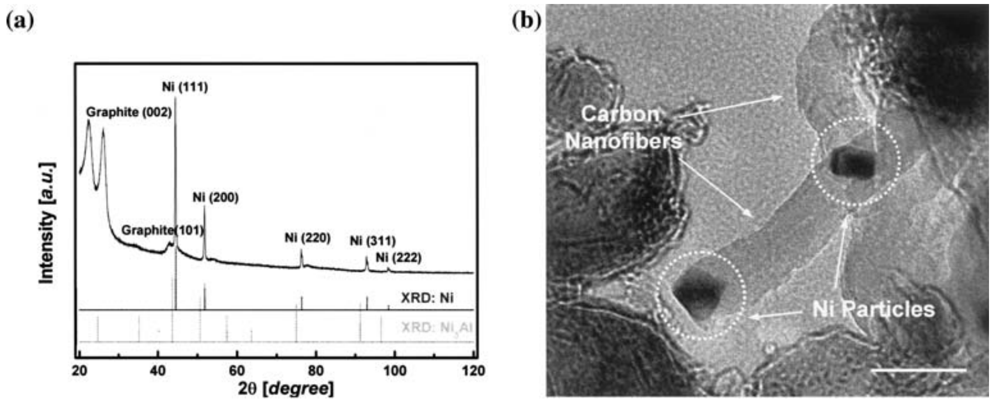

Figure 3. Characterization for surface products. (a) X-ray diffraction patterns for surface products on Ni_3Al foils after reaction at 793 K for 7 h. (b) Transmission electron micrograph for surface products on Ni_3Al foils after reaction at 793 K for 7 h. The scale bar represents 100 nm.

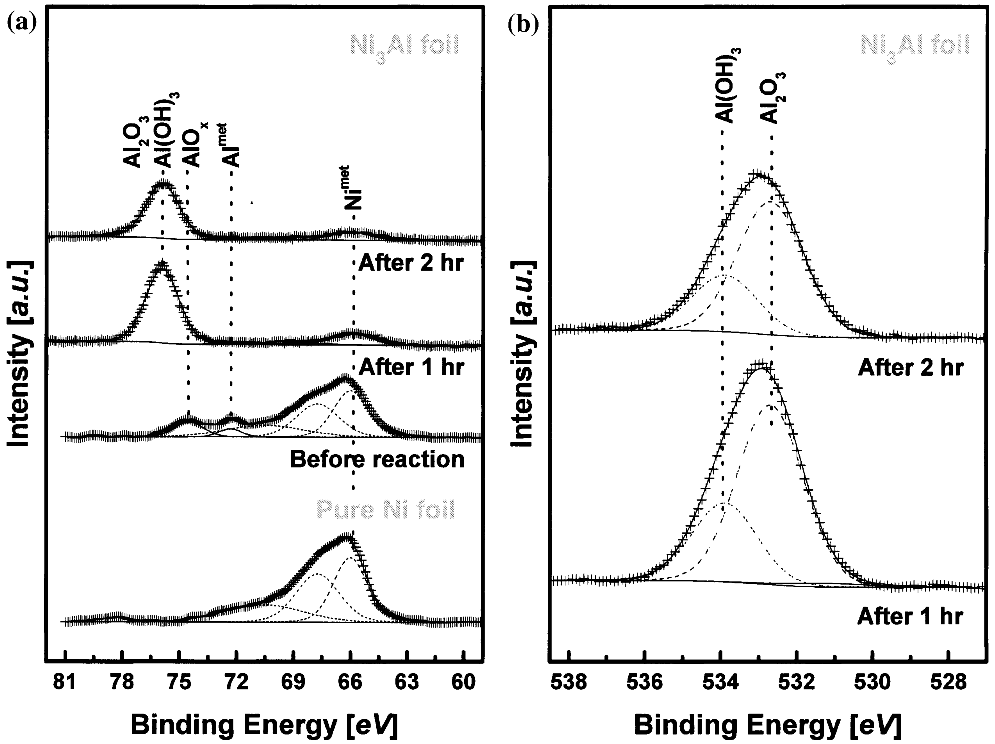

Figure 4. XPS spectra obtained over Ni_3Al foils at different period of reaction time at 793 K. (a) Al2p/Ni3p spectra for Ni_3Al foils before reaction, after 1 h of reaction, and after 2 h of reaction. For easy comparison, the spectrum of Ni foils was also inserted. (b) O1s spectra for Ni_3Al foils after 1 h of reaction and after 2 h of reaction.

show that Al in Ni_3Al is selectively oxidized and hydroxylated to form Al_2O_3 and $Al(OH)_3$ within the first 1 h. Fine Ni particles also form simultaneously (figure 2b). Considering that H_2 and CO are major products, the reaction atmosphere is highly reducing, and thus the Al_2O_3 can be γ-Al_2O_3 because it forms on the surface of Ni_3Al at low oxygen pressure [21,23]. $Al(OH)_3$ was probably produced through the reaction between products, i.e., Al_2O_3 and a small amount of H_2O [22].

The XPS results indicate that the formation of the fine Ni particles can be attributed to the selective oxidation and hydroxylation of Al. When Al is selectively oxidized and hydroxylated, Ni atoms are left behind and aggregate into fine particles [23,24], as shown in figure 2b. This process must occur in the first 1 h of the reaction. We think that the fine Ni particles serve as a catalyst for two reactions in the present study. First, they accelerate the methanol decomposition, leading to the increase in methanol conversion (figure 1). At the same time they accelerate the carbon precipitation from gaseous products, CH_4 or CO, leading to the carbon nanofibers forming (figure 3b).

Carbon deposition is normally detrimental to catalytic reactions: deposited carbon blocks the active sites of catalysts and decreases the activity. Such deactivation occurs during the methanol decomposition over Cu- or Cu/Cr-based catalysts [25]. However, almost no deactivation occurs in the Ni_3Al foils while carbon nanofibers form (figure 1). The deposited carbon on the Ni particles possibly diffuses to grow in the form of a fibrous structure, maintaining the surface of the Ni particles free of deposited carbon, as previously pointed out [26]. In addition, based on the morphology, we think that the produced carbon nanofibers suppress the coalescence of the Ni particles, acting as a means of support for heterogeneous catalysts [18–20]. These mechanisms may contribute to maintaining the catalytic activity and selectivity of the Ni particles during the reaction.

4. Conclusion

The catalytic properties of Ni_3Al foils for methanol decomposition were studied in the temperature range of 513–793 K. The following results were obtained. These results indicate that Ni_3Al foils can serve as catalyst precursors for methanol decomposition. Furthermore, they can serve as structural materials of microreactors as previously demonstrated [27]. In other words, a considerable part of microreactors for hydrogen production can be fabricated from Ni_3Al foils alone.

(1) The catalytic activity over the Ni_3Al foils rapidly increases with the increase of reaction time at 793 K during the first several hours of reaction, and stabilizes at high values during the subsequent reaction.

(2) A porous structure of carbon nanofibers including Ni particles forms on the surface of Ni_3Al foils during the reaction. It is suggested that these surface products enhance the activity and stability for methanol decomposition.

Acknowledgements

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