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Enhanced catalytic activity of Ni₃Al foils towards methane steam reforming by water vapor and hydrogen pretreatments

Ya Xu^{a,*}, Yan Ma^b, Masahiko Demura^a, Toshiyuki Hirano^a

^a Hydrogen Materials Unit, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

^b North China Electric Power University, 2 Beinong Rd., Huilongguan, Changping District, Beijing 102206, China

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ABSTRACT

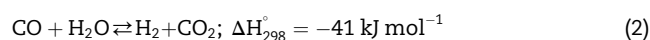
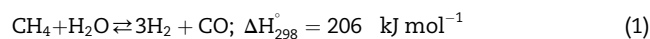
A pretreatment procedure consisting of water vapor oxidation followed by H₂ reduction has been developed for enhancing the catalytic activity of as-rolled Ni₃Al foils for steam reforming of methane. The catalytic activities of the as-rolled Ni₃Al foils in the temperature range of 873–1023 K at a steam to carbon ratio of 1.0 were found to be significantly improved by the pretreatment procedure consisting of a water vapor oxidation at 873–923 K for 1 h followed by a H₂ reduction at 873 K for 1 h. Surface characterization of the foils before and after the reactions revealed that many fine NiO particles were formed on the surface by the water vapor oxidation at 873–923 K, whereas much less NiO particles were formed by the water vapor oxidation at low temperatures (<873 K) or high temperatures (>973 K). During the subsequent H₂ reduction treatment at 873 K, these NiO particles were reduced to metallic Ni. It is supposed that the enhancement in catalytic activity is attributed to the fine metallic Ni particles formed on the foil surface by the pretreatment procedure.

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Introduction

With the rapid development of hydrogen fuel cells worldwide, hydrogen is attracting significant attention as a non-polluting and efficient energy carrier. Producing hydrogen at a low cost and with high efficiency is a great challenge in the field of catalysis [1–5]. Currently, hydrogen is mainly produced from various hydrocarbons such as methane, naphtha, and diesel.

Among these methods, the steam reforming of methane, which involves the following reactions (Eqs. (1) and (2)), is one of the most important methods [6,7].



Eq. (1) is known as methane steam reforming (MSR),

Abbreviations: MSR, methane steam reforming; WGS, water gas shift reaction; GHSV, gas hourly space velocity; SEM, scanning electron microscopy; EDS, energy dispersive X-ray spectroscopy; SE image, secondary electron image; BE image, backscattered electron image; TPR, temperature-programmed reduction; GC, gas chromatographs; TCD, thermal conductivity detector; XRD, X-ray diffraction; XPS, X-ray photoelectron spectroscopy.

* Corresponding author. Tel.: +81 298592573; fax: +81 298592501.

E-mail address: XU.Ya@nims.go.jp (Y. Xu).

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whereas Eq. (2) is the water gas shift reaction (WGS). Since MSR is highly endothermic, high temperatures (>1000 K) are required to achieve high CH₄ conversion to H₂ and CO. It is important to develop the steam reforming processes of CH₄ at low temperatures (<1000 K) in order to realize hydrogen production with high-efficiency and low-cost [3,8]. Ni-based catalysts have been developed for the steam reforming of CH₄ on the industrial scale [9]. In such catalysts, Ni particles, which are dispersed on refractory alumina carriers, are usually pelletized to optimized shapes to achieve good catalytic performance. The heat transfer efficiency and pressure drop are known to be limiting factors in the pelletized catalysts. On the other hand, structural catalysts such as monolithic and honeycomb catalysts are promising candidates for achieving high heat transfer efficiency and low pressure drop compared to the pelletized catalysts [10,11]. In the structural catalysts, the catalytic materials are deposited or dispersed on metallic or ceramic walls of the channels. However, this process is usually complex and results in high manufacturing costs.

The intermetallic compound Ni₃Al has excellent high-temperature strength, and has been used in superalloys as a strengthening phase [12,13]. We have fabricated thin foils of Ni₃Al with thickness below 30 μm by cold rolling [14,15], and found that these foils show high catalytic activity for methanol decomposition [16,17]. The results demonstrated that the Ni₃Al foils can be used as both catalysts as well as structural materials in the structural catalysts. This is favorable for practical applications because it allows efficient H₂ production without the need for a complex coating process for the catalyst layers, which in turn is expected to lead to low-cost and highly efficient hydrogen production. The catalytic activity of atomized Ni₃Al powder for MSR has been investigated in our previous work [18,19]. However, the catalytic properties of the Ni₃Al foils for MSR have not been examined yet.

In general, enhancing the catalytic activity of the flat foils is a challenging problem because of their extreme low specific surface area compared to fine particle catalysts. Interestingly, in our previous study on the catalytic properties of Ni₃Al foils for methanol decomposition, we found that the Ni₃Al foils were spontaneously activated during the initial period of reaction at 793 K [17]. The activation is attributed to the fine Ni particles formed on the foil surface during methanol decomposition. Specifically, the Al atoms in the surface region of the foils were oxidized and/or hydroxylated by a small amount of H₂O produced during the reactions, whereas the Ni atoms were not oxidized, and aggregated into the fine particles [20]. Furthermore, we have found that the surface structure of the Ni₃Al foils can be effectively modified by water vapor treatment at 873 K followed by H₂ reduction at 873 K [21]. This treatment procedure results in the formation of a pseudo porous structure constituted of Ni particles, Al₂O₃, and NiAl₂O₄ on the foil surface. This structure is expected to enhance the catalytic activity of the Ni₃Al foils.

In this study, we first examined the catalytic properties of the as-rolled Ni₃Al foils for MSR. Subsequently, we carried out a pretreatment procedure consisting of water vapor treatment at various temperatures, followed by H₂ reduction at 873 K for 1 h, in order to enhance the catalytic performance at low temperatures (<1000 K). The effect of pretreatment on the

surface structure and catalytic properties of MSR was investigated.

Experimental

Sample preparation

Ni₃Al (Ni-24 atomic % Al) foils with a thickness of 30 μm were fabricated by a cold-rolling procedure which has been described previously [14,15]. The samples for the reactions were cut into 5 mm × 220 mm rectangular pieces, which were then crinkled and wound in a spiral shape (coil) with a diameter less than but close to 8 mm (as shown in Fig. 1).

Pre-treatments

The water vapor and H₂ reduction treatments were carried out in a conventional fixed-bed flow reactor which has been described in our previous work [17,21]. The samples were first heated to 773, 823, 873, 923, 973, 1073 K, respectively under flowing N₂ at 30 mL/min, following which water was introduced using a micro-pump at a liquid flow rate of 50 μL/min for 1 h in the presence of flowing N₂. The partial pressure of water vapor in the reactor was 68 kPa during the water vapor treatment. Then, H₂ reduction was carried out at 873 K for 1 h in a flow of mixed H₂ (5 mL/min) and N₂ (30 mL/min), which is a common pre-reduction condition for Ni₃Al catalysts [18,19].

Catalytic reaction tests

Three coil samples with a total geometrical surface of 0.0066 m² were used for each test. The MSR tests were carried out over the as-rolled (non-pretreated) and pretreated foils (after treatment by the water vapor and H₂ reduction procedures) in the fixed-bed flow reactor. Two types of tests, namely isochronal and isothermal tests, were carried out as

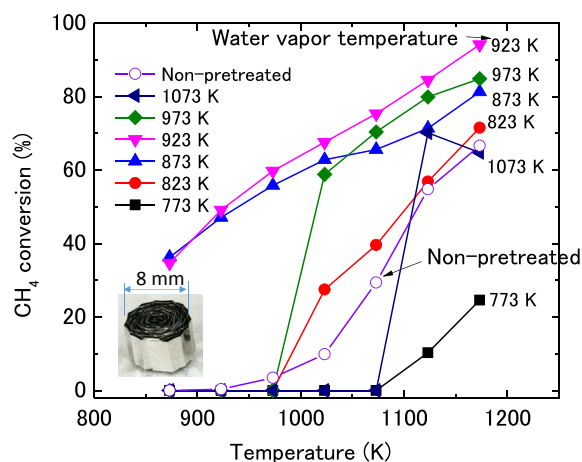


Fig. 1 – CH₄ conversion as reaction temperature during the steam reforming of CH₄ over non-treated Ni₃Al foils, and the foils pretreated in water vapor at 773, 823, 873, 923, 973, 923, and 1073 K for 1 h, respectively. All the foils were reduced by H₂ at 873 K for 1 h before reaction. The image of coil-shaped sample for reaction was inserted.

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