

Effect of surface pretreatment on the catalytic activity of atomized Ni₃Al powder for methane steam reforming

Yan Ma^{1,2}, Ya Xu¹, Masahiko Demura¹, and Toshiyuki Hirano^{1,2}

¹National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

² University of Tsukuba, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
Fax: 81-029-859-2501; e-mail: ma.yan@nims.go.jp

Catalytic experiments were performed over atomized Ni₃Al powder in the temperature range from 873 to 1223 K under the atmosphere of steam and methane (ratio of 1). The powder was treated by two kinds of two-step surface pretreatment before reaction. One is chemical treatment, acid leaching followed by alkali leaching. Another is steam treatment, oxidization in steam followed by reduction in hydrogen. It was found that the catalytic activity was significantly enhanced by both pretreatments, especially by the chemical treatment. The surface characterization of the pretreated powders revealed that the enhancement by the pretreatments was attributed to the formation of fine Ni particles on the surface.

Key words: Ni₃Al, surface pretreatment, catalytic activity, methane steam reforming.

1. INTRODUCTION

Methane steam reforming (MSR) is the most dominant reaction in producing hydrogen nowadays [1, 2]. Nickel-based catalysts are widely used for this chemical process [3]. However, their performance is not satisfactory and more efficient catalysts are required [4].

In Ni-Al system there are four stable compounds, namely NiAl₃, Ni₂Al₃, NiAl and Ni₃Al. Among them, a mixture of NiAl₃ and Ni₂Al₃ is used as a precursor alloy for Raney nickel catalysts [5, 6]. Raney nickel catalysts are produced from this precursor alloy by selectively leaching aluminum in a concentrated NaOH solution. For Ni₃Al, it has never been used as the precursor alloy of Raney nickel catalysts, probably because it was thought to be difficult to effectively leach aluminum out due to its low aluminum concentration. Thus, a high catalytic activity has not been expected [7].

Ni₃Al intermetallic compound is well known as an excellent high-temperature structural material because of its high-temperature strength and good corrosion/oxidation resistance [8, 9]. Recently, our group for the first time found the catalytic activity in Ni₃Al for MSR by using its atomized powder. It was found that the activity

was effectively enhanced by a combined chemical surface pretreatment of acid and alkali leaching, while it was quite low for the as-received powder [10]. The result suggests a potential of Ni₃Al as catalytic precursor for MSR. The interesting thing is that the enhancement is attributed to the formation of fine Ni particles on the surface.

In this study, we tested another pretreatment, steam treatment in order to form Ni particles on the surface. It consists of two steps: oxidation in steam and reduction in hydrogen. We expect that NiO forms in the first step and changes into Ni particles in the second step. We present the catalytic activity of the pretreated powder for MSR comparing the results in the combined chemical surface pretreatment mentioned above.

2. EXPERIMENTAL

The as-received Ni₃Al (Ni-25 at.% Al, 75-150 μm in diameter) powder is the same as that used in the previous study [10]. Since it was rapidly solidified during the atomizing process, it had a second phase in the Ni₃Al matrix which was identified as L1₀-type β'-NiAl by TEM analysis [10]. The as-received powder was pretreated in the following two ways before the catalytic experiments as listed in Table 1. Each

Table 1 Pretreatment process and the results of BET surface area measurement

	Process (a): Chemical treatment	Process (b): Steam treatment	As-received
Pretreatment process	Step 1: Acid leaching in 2 vol.% HNO ₃ , 298 K, 15 min Step 2: Alkali leaching in 20 wt% NaOH, 366 K, 300 min	Step 1: Oxidized in flowing steam, at rate of 30 ml/min, 873K, 1h Step 2: Reduced in flowing H ₂ 873 K, 1 h	Untreated
Surface area (m ² /g)	0.41	0.27	0.06

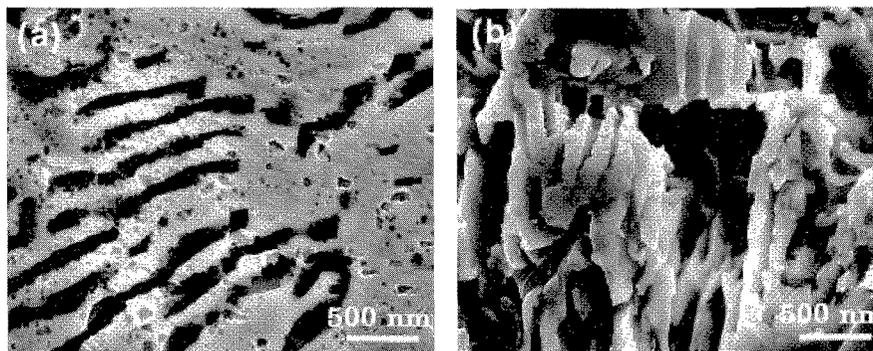


Fig. 1. SEM images of Ni₃Al powders after each step of the chemical treatment: (a) after step 1-acid leaching, showing selective leaching of β' phase; (b) after step 2-alkali leaching, showing formation of porous surface by selective leaching of Al [10].

pretreatment includes two steps. Process (a) is chemical pretreatment: step 1 is a dip treatment at 298 K for 15 min in 2 vol.% aqueous HNO₃, and the following step 2 is a dip treatment at 366 K for 300 min in a stirred 20 wt% aqueous NaOH solution. Process (b) is steam pretreatment: step 1 is an oxidation treatment in flowing steam at rate of 30 ml/min at 873 K for 1 h, and the following step 2 is a reduction treatment in flowing H₂ for 1 h. After these treatments the surface area of the powders was determined by the Brunauer-Emmett-Teller (BET) surface area analysis method using krypton adsorption (Micromeritics, ASAP 2020). The surface morphology was observed by scanning electron microscopy (SEM: JEOL, JSM-7000F). The crystal structure of the surface were analyzed by X-ray diffraction (XRD) using a Cu K α source (Rigaku, RINT2500).

The catalytic experiments were carried out in a conventional fixed-bed flow reactor in the same way as described in previous reports [10]. Prior to the reaction, the powder was reduced at 873 K for 1 h in a flowing hydrogen atmosphere. The hydrogen flow was then stopped and filled with pure nitrogen to flush the hydrogen. Subsequently, mixed reactants of CH₄ and H₂O (mole ratio of H₂O/CH₄=1) were introduced into the quartz tube reactor at the gas hourly space velocity of 12000 h⁻¹ (defined as the volume of CH₄ passed over the unit volume of catalyst per hour). Finally, the temperature was stepwise increased from 873 to 1173 K at intervals of 50 K. The composition of the outlet gas products was analyzed after a lapse of 30 min at each temperature using a gas chromatograph (GL Science, GC-323 equipped with thermal conductivity detectors). The total flow rate of the gas products was measured at each temperature using a soap bubble meter just after the gas analysis.

3. RESULTS AND DISCUSSION

3.1 Characterization of pretreated powder

The BET surface area measurement was carried out on the as-received and pretreated powders and the

results are summarized in Table 1. The surface area of as-received powder is very small, only 0.06 m²/g. The surface area increased by the chemical treatment more effectively than that by the steam treatment. The surface area is about seven times of that of the as-received powder after the chemical treatment and about four times after the steam treatment.

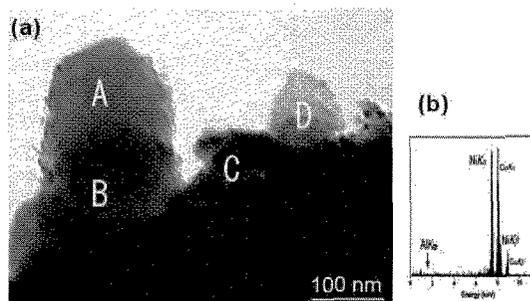


Fig. 2 (a) TEM bright field image after chemical pretreatment, showing the formation of the fine particles on the surface, and (b) EDS spectra taken from position B, showing the particles are composed of pure Ni (TEM sample was supported on a copper mesh) [10].

Fig. 1 shows the SEM images of the surface of atomized Ni₃Al powder after the chemical pretreatment, showing the evolution of surface morphology during the process [10]. As described in Section 2, the as-received powder contained β' -NiAl in the Ni₃Al matrix. It is clearly shown in Fig. 1 (a) that the β' -NiAl was selectively dissolved by the step 1 of acid leaching, leaving a lamellar porous structure on the surface. Thus, the surface area was effectively increased. After the step 2 of alkali leaching, Al atom was selectively dissolved in the aqueous NaOH solution, which made the surface Ni-enriched similar to the case in preparation of Raney nickel catalysts [5, 6]. The step 2 also contributed to make the surface more porous as shown in Fig. 1 (b). In spite of this drastic surface change, no structure changes were detected by XRD after the chemical pretreatment, which indicated that the treatment was limited to the thin surface layer of the powder. TEM analysis was carried out to examine the outmost surface of the powder as shown in Fig. 2. The bright field image (Fig. 2(a)) shows

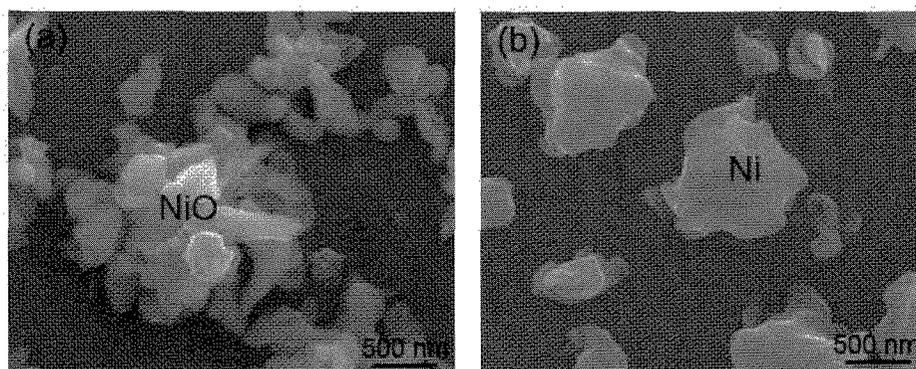


Fig. 4. SEM images of Ni_3Al powders after each step of the steam treatment: (a) after step 1-oxidation, showing formation of NiO on the surface; (b) after step 2-reduction, showing formation of pure Ni particles on the surface.

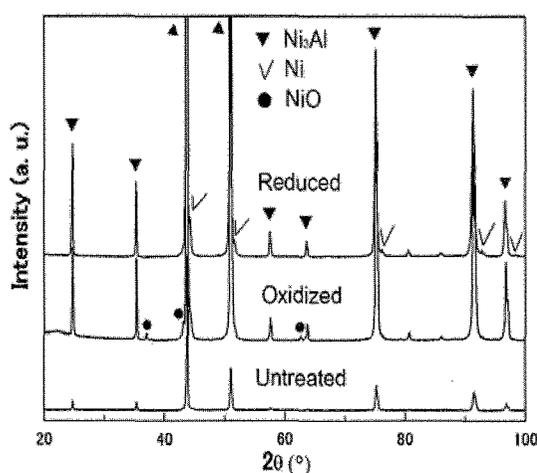


Fig. 3. XRD pattern of Ni_3Al powder after each step of the steam pretreatment: (a) after step 1 – oxidation, showing formation of NiO, and (b) after step 2 - reduction, showing formation of pure Ni.

many particles are formed on the surface. The EDS spectra were taken from the position A, B, C and D in Fig. 2 (a). All the spectra were quite similar. The spectra obtained from the position B revealed that the particles are composed of almost pure Ni. Therefore, it turned out that the structure of fine Ni particles dispersed on the surface of the Ni_3Al powder was produced by the chemical pretreatment.

The evolution of the surface structure and morphology during the steam pretreatment was examined by XRD (Fig. 3) and SEM (Fig. 4). After the step 1 of oxidation in steam, NiO diffraction peak was clearly identified. After the step 2 of reduction in hydrogen, NiO peaks disappeared and Ni peaks appeared instead. SEM images in Fig. 4 show the surface morphology after each step of the steam treatment. Fig. 4(a) shows the formation of NiO particles after step 1 corresponding to Fig. 3 and Fig. 4(b) shows the formation of Ni particles after step 2 which were confirmed by SEM-EDS (not shown here). Therefore, it is found that pure Ni particles were formed on the surface of Ni_3Al powder by the steam treatment. Based

on the examination by SEM, TEM and XRD, obviously, the mean size of the Ni particles is much larger than those formed by the chemical treatment. Also, the powder surface is rather smooth. Thus, the BET surface area pretreated by the steam treatment is smaller than that pretreated by the chemical treatment as shown in Table 1.

3.2 Catalytic activity

The catalytic activity over the untreated and pretreated Ni_3Al powders for MSR was isochronally measured under the conditions of pressure=1.013 bar and S/C=1 from 873 to 1223 K. Three gaseous products, H_2 , CO and CO_2 , were detected at the reactor outlet by gas chromatography. Fig. 5 plots the production rates of H_2 , CO and CO_2 as a function of the reaction temperature.

The effect of surface pretreatment is remarkable in the hydrogen production rate (Fig. 5 (a)). Hydrogen is not produced over the untreated as-received powder until the temperature increases up to 1173 K. However, the onset temperature of catalytic activation is significantly reduced to below 873 K by the both two pretreatments. Particularly, the effect is more clearly observed in the chemical treatment than in the steam treatment. Carbon monoxide and carbon dioxide were also produced over the powder after both pretreatments from the low temperature (Fig. 5 (b) and (c)). From the Fig. 5, it is clear that the production rates of H_2 and CO increase monotonously with increasing temperature, while the production rate of CO_2 decreases with temperature. However, the differences of the production rates of H_2 and CO between two pretreated powders at the temperature below 973 K are smaller than those at high temperature, especially for CO production rate. Furthermore, the CO_2 production rate for chemically treated powder is higher than that of steam treated powder at low temperature and reverses at high temperature.

As pointed out in the previous studies on the

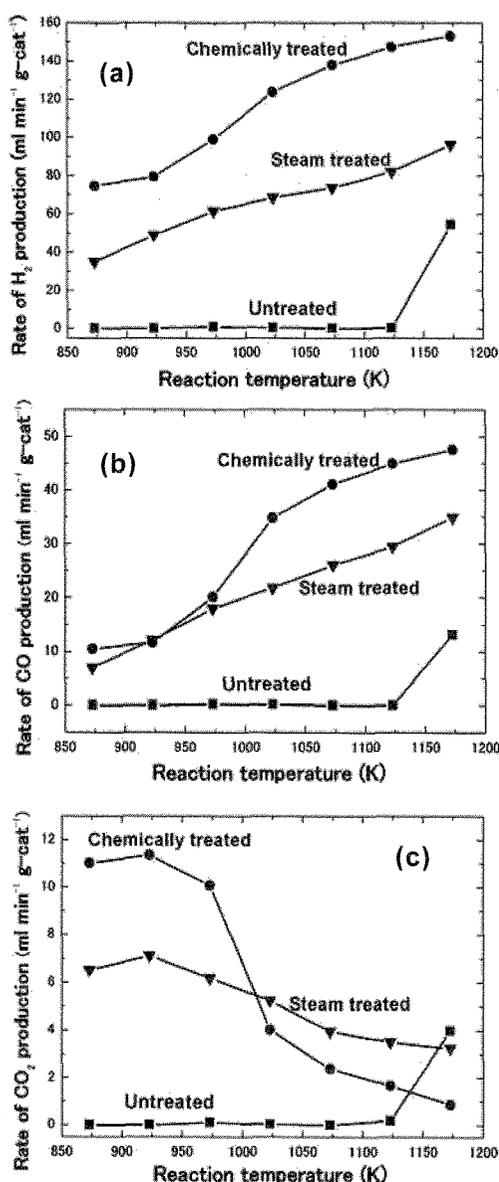
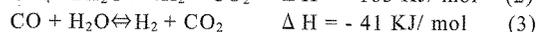


Fig. 5 Production rates of (a) H₂, (b) CO, and (c) CO₂ by methane steam reforming over the chemically pretreated, steam pretreated and untreated Ni₃Al powders (S/C=1, P=1.013bar).

kinetic of MSR [11, 12], the following three chemical reversible reactions are considered to be involved: the strongly endothermic reforming reaction (1) and (2), and the moderately exothermic water-gas shift reaction (3):



Due to its endothermic character, the two reforming reactions are favored by high temperature. In contrast, the exothermic water-gas shift reaction is favored by low temperature. In brief, the temperature dependences of the three production (H₂, CO and CO₂) rates over the pretreated Ni₃Al powders are both understood based on the thermodynamic of

the MSR. As is well known fine Ni particles are catalytically active for MSR [4]. The results in Section 3.1 revealed that nickel particles were formed on the powder surface after both two pretreatments, and their size was much smaller in the chemical treatment than the steam treatment (Figs. 2 and 4). Therefore, the differences in the size of Ni particles and the surface area are considered to reflect on the large difference in the catalytic activity between the two treatments. The detailed analysis is in progress.

4. CONCLUSIONS

The catalytic activity of atomized Ni₃Al powder for MSR was tested from 873 to 1223 K under S/C= 1. Two kinds of surface pretreatments, namely chemical treatment and steam treatment, were carried out on the powder. The results are summarized as follows.

(1) The activity of atomized Ni₃Al powder was significantly enhanced by both two surface pretreatments.

(2) The enhancement was attributed to the formation of fine Ni particles on the surface in both the treatments.

(3) The higher activity was obtained by the chemical treatment than by the steam treatment, which possibly due to the larger surface area and smaller Ni particles produced by this pretreatment.

(4) The results indicate that Ni₃Al is highly promising as catalyst precursor for MSR.

REFERENCES

- [1] J. N. Armor, *Catal. Lett.*, 101, 131-35 (2005).
- [2] G. W. Crabtree, M.S. Dresselhaus, and M.V. Buchanan, *Physics Today*, 57 (12), 39 (2004).
- [3] J. R. Rostrup-Nielsen, "Catalysis, Science and Technology", Vol. 5, Ed. by J. R. Anderson, M. Boudart, (Springer, Berlin, 1984) ch. 1.
- [4] J. R. Rostrup-Nielsen, J. Sehested, and J. K. Nørskov, *Adv. Catal.*, 47, 65-139 (2002).
- [5] G. Ertl, "Preparation of Solid Catalysts", Ed. by M. S. Wainwright, Wiley-Vch, New York, (1999) pp.29-31.
- [6] M. Raney, 162810-, US Patent, 1927.
- [7] S. Tanaka, N. Hirose, T. Tanaki, and Y. H. Ogata, *J. Electrochem. Soc.*, 147, 2242-45 (2000).
- [8] C. T. Liu and D. P. Pope, "Intermetallic Compounds -Practice-", Vol. 2, Ed. by J. H. Westbrook and R. L. Fleischer (John Wiley & Sons, Chichester, 1995), p.17-51.
- [9] D. B. Miracle and R. Darolia, in: *Intermetallic Compounds -Practice-*, Vol. 2, eds. J. H. Westbrook and R. L. Fleischer (John Wiley & Sons, Chichester, 1995), p.53-72.
- [10] Y. Ma, Y. Xu, M. Demura, D. H. Chun, G. Q. Xie and T. Hirano, *Catal. Lett.*, 112, 31-36 (2006).
- [11] J. Xu and G.F. Froment, *AICHE J.*, 35 (1) 88, (1989).
- [12] M. A. Soliman, A. M. Adris, A. S. Al-Ubaid and S. S. E. H. El-Nashaie, *J. Chem. Tech. Biotechnol.*, 55, 131 (1992).