Catalytic Activity Improvement of Ni/SnO₂ Nanoparticles Dispersed on Nickel Alloy for Hydrogen Generation

Wenlong Song^{a,b*}, Dan Li^{a,b}, Lu Shi^{a,b}, Weiwei Zeng^a, Hao Yin^a, Donglai Li^a, Jiasong Chang^a, Luxi Yao^a, Liyan Huang^a, Meiqiang Fan^{a,b*}

^aDepartment of Materials Science and Engineering, China Jiliang University, Hangzhou 310018, P R China, E-mail: Sah003@yeah.net, queenfree123@126.com

^bZhejiang Tianneng Energy Technology Co., Ltd., Changxing County, Zhejiang Province 313100, China

Abstract: The activity of Ni₃Sn powder after oxidation-reduction treatment was investigated for producing hydrogen from methanol under different conditions. The treated Ni₃Sn powder, especially that the Ni₃Sn oxidized at higher temperature showed a much higher activity than non-treated Ni₃Sn; compared to Ni₃Sn oxidized at 1073 K, Ni₃Sn oxidized at 1373 K showed 10 times higher H₂ and CO generation rates, but similar low CO₂ and CH₄ generation rates. The activity of treated Ni₃Sn significantly increased with increasing oxidation temperature and decreasing reduction temperature. The activity improvement of treated Ni₃Sn powder was attributed to the formation of fine nanostructured Ni/SnO₂ particles, which were supposed to be the cause of the improved activity of Ni₃Sn.

Key words: Oxidation-reduction; methanol decomposition; hydrogen production;

Ni/SnO₂ catalyst; microstructure

1. Introduction

Methanol is a potential hydrogen source because it has low cost and high H/C atomic ratio [1]. Many catalysts have been developed for large-scale hydrogen production from methanol in the past twenty years, including Pt-, Rh-, Ni- and Co-based catalysts [2-5]. The catalysts effectively decreased the formation of methane, water, carbon, and other byproducts from methanol. However, the development of highly efficient, recyclable, and cheap catalysts is still required.

Ni₃Sn-based composite is a known catalyst with high selectivity [6-9], as it can suppress methane or carbon production during hydrocarbon reforming. But the catalytic properties of single-phase Ni₃Sn intermetallic compound was seldom evaluated, especially for methanol decomposition [10, 11]. It was reported that the activity of Ni₃Sn was not high and only 2.4% methanol conversion was achieved for Ni₃Sn intermetallic compound particles at 713 K [12]. The oxidation-reduction method may be effective in improving the activity of Ni₃Sn. In the previous work [13], a two-step pretreatment including oxidation in air followed by reduction in hydrogen, was effective for improving the catalytic activity of Ni₃Al foils for methanol decomposition via the formation of metallic Ni on an Al oxide layer on the surface. This demonstrated that the nanostructure formation of fine Ni dispersed on alumina was the key factor for the improved catalytic activity.

In this study, in order to enhance the activity of Ni₃Sn, we carried out oxidation of Ni₃Sn powders in air at 1073 K and 1373 K, subsequently reduced them in hydrogen, and then examined their catalytic properties for methanol decomposition

at different temperatures. The microstructure and surface changes of the catalyst were investigated before and after oxidation and reduction in order to understand the potential activation mechanism, which might be useful for the design of high-performance Ni_3Sn in the future.

2. Experimental

Single-phase Ni_3Sn powder was used as the starting material, which was oxidized in air at 1073 K and 1373 K for 5 h, respectively. The oxidized Ni_3Sn particles were reduced for 1 h at 773 K in 95% N_2 /5% H_2 atmosphere prior to catalytic activity test if no other reduction temperatures were stated. The catalytic properties were performed via isochronal and isothermal tests which were introduced in the previous work [11, 12]. Isothermal tests were performed at 713 K for non-treated Ni_3Sn and at 603 K for Ni_3Sn after oxidation at 1373 K with reduction for 1 h at 603 K.

The crystal structures of Ni_3Sn after oxidation and reduction were characterized by X-ray diffraction (XRD) using a Rigaku RINT 2500 with a $\text{CuK}\alpha$ source. The surface morphologies and compositions of the samples were analyzed by scanning electron microscopy (SEM, JEOL, JSM-7000F) with energy dispersive X-ray spectroscopy (EDS). The Brunauer-Emmett-Teller (BET) surface areas of the samples were measured by a surface-area analyzer (Micromeritics, ASAP2020) with N_2 as the adsorbent. The temperature programmed reduction (TPR) experiments were performed from 298 K to 973 K in a H_2 atmosphere with a heating rate of 5 K/min.

3. Results and discussion

3.1 Catalytic properties

Figure 1 shows methanol conversion changed with methanol decomposition temperature for Ni₃Sn before and after oxidation–reduction treatment. Non-treated Ni₃Sn showed low methanol conversion < 10% at 593–793 K. However, Ni₃Sn after oxidation–reduction treatment showed significantly improved catalytic activity. Ni₃Sn oxidized at 1073 K displayed 6% and 41% methanol conversion at 593 K and 793 K, respectively. Ni₃Sn oxidized at 1373 K exhibited 11% and 73% methanol conversion at the same temperatures, respectively. Oxidized Ni₃Sn showed much higher methanol conversion with increasing oxidation temperature, especially above 593 K. The results indicated that the catalytic activity of oxidized Ni₃Sn was higher than non-treated Ni₃Sn.

Figure 2 shows the production rates of various gases changed with methanol decomposition temperature for Ni₃Sn before and after oxidation–reduction treatment. The main products were H₂ and CO, and the production rates increased with temperature for all three samples. In contrast, the production rates of byproducts CH₄, CO₂ and H₂O were almost zero in the temperature range 593–793 K for all samples, reflecting their good selectivity for H₂ and CO in methanol decomposition. However, the production rates of H₂ and CO over non-treated Ni₃Sn were very low compared to the treated Ni₃Sn samples. The highest production rates of H₂ and CO over the non-treated Ni₃Sn samples were 22 and 10.5 mmol/h.g cat at 793 K, respectively. The production rates of H₂ and CO at 793 K over Ni₃Sn after oxidation at 1073 K and

1373 K were 298 and 149 mmol/h.g cat , and 396 and 201 mmol/h.g cat, respectively. These results indicated that the oxidation temperature increase of Ni₃Sn was effective in enhancing the production rates of H₂ and CO while keeping the production rates of byproducts CH₄, CO₂ and H₂O low.

The effect of reduction temperature following oxidation on the catalytic activity was examined and the detailed temperatures were selected via the TPR results of Ni₃Sn after oxidation at 1373 K in the followed section. Figure 3 shows methanol conversion changed with methanol decomposition temperature for oxidized Ni₃Sn before and after reduction at 603 K and 773 K. There was almost no methanol conversion over oxidized Ni₃Sn below 553 K. However, after increasing the reaction temperature from 553 K to 633 K, methanol conversion over oxidized Ni₃Sn was quickly enhanced from 0 to 80.7%, and remained at approximately 80% as the temperature increased from 633 K to 793 K. The results revealed that oxidized Ni₃Sn had good catalytic activity above 553 K. After reduction at 603 K, oxidized Ni₃Sn showed 3.5% and 9.1% methanol conversion at 513 K and 553 K reaction temperature. Methanol conversion over oxidized Ni₃Sn after reduction at 603 K steadily increased from 3.5% to 76.6% as the reaction temperature increased from 513 K to 793 K. After reduction at 773 K, oxidized Ni₃Sn displayed 1.5% and 4.5% methanol conversion at 513 K and 553 K reaction temperature. Methanol conversion over oxidized Ni₃Sn after reduction at 773 K steadily increased from 1.5% to 68.8% as the reaction temperature increased from 513 K to 793 K. These results showed that after reduction, oxidized Ni₃Sn had low catalytic activity below 553 K, and that the

catalytic activity decreased above 553 K with increasing reduction temperature.

Isothermal tests were performed over treated and non-treated Ni_3Sn at 603 and 713 K, respectively, to examine their catalytic properties in more detail. The treated Ni_3Sn was oxidized at 1373 K and reduced for 1 h at 603 K. Figure 4 shows the methanol conversions over the catalysts as a function of time on the stream. Approximately 2.3% methanol was converted over Ni_3Sn when the test started, which increased to approximately 2.4% after 28 h. In contrast, the conversion of methanol over treated Ni_3Sn at 603 K reached 31% in the first 20 min, and then slowly decreased with time on the stream. Nevertheless, it reached 17% after 28 h, which was approximately 7 times than that over non-treated Ni_3Sn at 713 K. These results revealed that Ni_3Sn after oxidation- reduction treatment had a much higher catalytic activity than that of non-treated Ni_3Sn .

3.2 Catalyst characterization

Figure 5 shows the TPR profiles for the Ni_3Sn samples after oxidation at 1073 K and 1373 K. There were three significant reduction peaks for oxidized Ni_3Sn , which had different reduction temperatures. As for Ni_3Sn after oxidation at 1073 K, the reduction peak at 673 K refers to the reaction of NiO to Ni [14]. The reduction peak starting at 623 K that overlaps with another peak at 723 K might be due to the reaction of SnO_2 to SnO ; the other at 773 K was the reaction of SnO to Sn [15]. For Ni_3Sn after oxidation at 1373 K, the reaction of NiO to Ni started at 563 K and the reduction continuously occurred at the subsequent temperatures. The reduction peak of SnO_2 to SnO occurred at 773 K and that of SnO to Sn was at 933 K. The reduction

temperature of NiO to Ni reduced by approximately 60 K, and the reduction peaks of SnO₂ to SnO and SnO to Sn increased by approximately 100 K. The reduction peak intensity increased for Ni₃Sn with increasing oxidation temperature (1073 to 1373 K). This might be due to an increased amount of Ni or Sn oxide, as more Ni₃Sn was oxidized at high temperatures. The TPR results were related to the stability of oxides and were important for the selection of reduction temperatures.

Figure 6 shows the XRD patterns of Ni₃Sn before and after oxidation. The initial XRD patterns were obtained using prepared Ni₃Sn powders before oxidation, and only diffraction peaks attributed to Ni₃Sn (hexagonal, P63/mmc) were identified. The XRD patterns obtained for both Ni₃Sn samples after oxidation at 1073 and 1373 K were partially identical to the initial XRD patterns, but there were also some peaks attributable to Ni₃Sn (cubic), and oxides of Ni or Sn. The results showed that a small amount of hexagonal Ni₃Sn might be transformed to cubic Ni₃Sn, and that some Ni₃Sn was oxidized at temperatures above 1073 K in air. There were new indistinct peaks observed at 30, 44 and 60° for NiO and SnO₂, as well as the main peaks for Ni₃Sn, in the XRD patterns for Ni₃Sn oxidized at 1073 K, indicating that Ni₃Sn was slightly oxidized at 1073 K. The peaks for NiO and SnO₂ became stronger in the XRD patterns of Ni₃Sn after oxidation at 1373 K.

Table 1 shows the BET surface areas (m²/g) of Ni₃Sn after oxidation. The specific surface area of Ni₃Sn powders was 0.07 m²/g before oxidation. The specific surface area significantly increased to 0.2 m²/g after oxidation at 1073 K, which was twice as high as that of Ni₃Sn. The Ni₃Sn oxidized at 1373 K had a specific surface

area of $0.5 \text{ m}^2/\text{g}$, which was five times that of Ni_3Sn .

The surface morphology of Ni_3Sn before and after oxidation was analyzed using SEM, and the results are shown in Figure 7. Ni_3Sn presented a relatively large smooth surface, with tens of μm in diameter, before oxidation. The surface changed significantly after oxidation. Following oxidation at 1073 K, a continuous granular oxide layer was formed on the surface. The grain size was several hundreds of nm in diameter, with well-developed flat facets. The dense oxide layer on the Ni_3Sn surface is expected to prevent the continuous oxidation of Ni_3Sn . However, the dense layer was destroyed and the particles were scattered significantly on the Ni_3Sn surface after oxidation at 1373 K. More Ni_3Sn was oxidized into Ni or Sn oxides, and the oxide particles became larger and showed different shapes (Figure 7c). Changes in the particle shape might be due to the partial melting of Ni_3Sn during oxidation at 1373 K, because the melting point of Ni_3Sn is near to 1250 K.

Figure 8 shows the XRD patterns of oxidized Ni_3Sn before and after reduction. Peaks for Ni_3Sn , NiO and SnO_2 were identified in the XRD patterns of Ni_3Sn before and after oxidation. After reduction at 603 K, new peaks for Ni were observed, as well as the original materials, showing that NiO was partly reduced. As the reduction temperature increased from 603 K to 773 K, the peaks for NiO disappeared and peaks for SnO were observed, as well as those of Ni_3Sn , Ni and SnO_2 . Table 2 shows the BET surface areas (m^2/g) of Ni_3Sn after oxidation-reduction. The oxidized Ni_3Sn powders had large specific surface areas of up to $0.5 \text{ m}^2/\text{g}$. The specific surface area increased to $0.9 \text{ m}^2/\text{g}$ for Ni_3Sn after reduction at 603 K, which was 1.8 times higher

than that of oxidized Ni₃Sn without reduction. With an increase in the reduction temperature to 773 K, oxidized Ni₃Sn had a specific surface area of 1.1 m²/g, which was two times higher than that of oxidized Ni₃Sn without reduction.

Figure 9 shows the surface morphologies of oxidized Ni₃Sn after reduction. Particles with different shapes and sizes were observed before reduction. After reduction at 603 K, the shapes of the particles were changed from flat to column-like. With a further increase in reduction temperature, more columns were observed. From a small area, the EDS results showed that the elemental oxygen atom% decreased from 50.3 atom% to 9.9 atom% as the reduction temperature increased. Obviously, the shape changes were attributed to the reduction of Ni/Sn oxides.

3.3 Activity analysis

These experimental results show that Ni₃Sn exhibits higher activity after oxidation-reduction treatment compared to non-treated Ni₃Sn, while retaining a high H₂ selectivity for methanol decomposition. The activity is enhanced with increasing oxidation temperature and decreasing reduction temperature (Figures 1–4). The enhancement is believed to be related to the formation of fine Ni/SnO₂ composites, which have been identified by XRD, SEM and EDS analyses. Fine Ni/SnO₂ particles were observed to be formed on the catalyst surface after oxidation and reduction, and the number of small particles increased at higher oxidation temperature, confirmed by the SEM and BET results. However, the SnO₂ particles are not stable and transformed into SnO at a higher reduction temperature (Figure 5, 8, 9). Combined with the catalytic test results shown in Figure 4, the reduction of SnO₂ to SnO on the catalyst

surface may slightly deactivate the catalyst. A significant change in microstructure is observed in Figure 10, in which new peaks for Ni and SnO were determined as well as those for Ni₃Sn, NiO, and SnO₂ in the XRD patterns of treated Ni₃Sn after the isothermal test at 603 K. The surface morphology and elemental distribution of treated Ni₃Sn after the isothermal test at 603 K are shown in Figure 11, in which the elemental oxygen atom% decreases significantly in comparison with that on the surface of treated Ni₃Sn. However, the BET results in Table 2 show that the specific surface area undergoes few changes before and after the thermal test at 603 K, indicating that there are no smaller particles or byproduct carbon generated in the methanol decomposition process. The results show that the reactions of NiO to Ni and SnO₂ to SnO occur on the surface of treated Ni₃Sn in methanol decomposition, and they are responsible for the high low temperature activity and deactivation of the catalyst, respectively. Therefore, determining how to obtain fine Ni/SnO₂ particles and retain their microstructure in methanol decomposition is important for future applications.

4. Conclusion

The catalytic properties of Ni₃Sn after oxidation and reduction were investigated for the decomposition of methanol in the range 513-793 K, and the following results were obtained:

1. The Ni₃Sn powders showed much higher catalytic activity after oxidation and reduction than that of non-treated Ni₃Sn. The enhancement of activity was affected by the oxidation and reduction temperatures; the catalytic activity

increased with increasing the oxidation temperature from 1073 to 1373 K, but decreased with increasing the reduction temperature from 603 to 773 K.

2. The Ni_3Sn powders gave higher production rates of H_2 and CO and retained very low production rates of CH_4 , CO_2 and H_2O after oxidation and reduction, compared with the non-treated Ni_3Sn sample over the whole temperature range. This indicated that treated Ni_3Sn had high selectivity for H_2 and CO .
3. Surface analysis suggested that Ni and Sn oxides were formed on the surface of Ni_3Sn during the oxidation process, and the specific surface area significantly increased with increasing oxidation temperature. The initial reduction temperature for NiO to Ni decreased, but the reduction temperature for SnO_2 to SnO and SnO to Sn increased as the oxidation temperature of Ni_3Sn increased from 1073 to 1373 K.
4. Fine Ni/SnO_2 particles were formed on the surface of oxidized Ni_3Sn after reduction treatment or during methanol decomposition. Their number increased with an increase in oxidation temperature. These fine Ni/SnO_2 particles are considered to contribute to the improved catalytic activity.

Acknowledgments

This work was financially supported by the Scientific Research Foundation for the Returned Scholars, postdoctoral support of P. R China (2015M581910), postdoctoral preferential support of Zhejiang province (BSH1502029), the National Science Foundation of China (Project No. 51501175), and the Guangxi Key Laboratory of Information Materials (Guilin University of Electronic Technology,

project No. 1210908-02-K).

References

- [1] L.F. Brown. A comparative study of fuels for on-board hydrogen production for fuel-cell-powered automobiles. *Int J Hydrogen Energy* 2001;26:381–397.
- [2] P. J. Wild, M.J. Verhaak. Catalytic production of hydrogen from methanol. *Catalysis Today* 2000;60:3–10.
- [3] J. C. Brown, E. Gulari. Hydrogen production from methanol decomposition over Pt/Al₂O₃ and ceria promoted Pt/Al₂O₃ catalysts. *Catalysis Communication* 2004;5: 431–436.
- [4] V. D. Santo, A. Gallo, A. Naldoni, M. Guidotti, R. Psaro. Bimetallic heterogeneous catalysts for hydrogen production. *Catalysis Today* 2012;197: 190–205.
- [5] T. Ohashi, Y. Wang, S. Shimada. Preparation and high catalytic performance of hollow BN spheres-supported Ni for hydrogen production from methanol. *J. Materials Chemistry*, 2010, 20: 5129-5135.
- [6] M. Lenarda, E. Moretti, L. Storaro, P. Patrono, et al. Finely dispersed Pd-Zn catalyst supported on an organized mesoporous alumina for hydrogen production by methanol steam reforming. *Appl Catal A: Gen* 2006;312:220–228.
- [7] J. W. Shabaker, D. A. Simonetti, R. D. Cotright, J. A. Dumesic. Sn-modified Ni catalysts for aqueous-phase reforming: Characterization and deactivation studies. *J Catal* 2005;231:67–76.
- [8] A. Penkova; L. Bobadilla; S. Ivanova; M. I. Dominguz; F. Romero-Sarria; A. C. Roger; M. A. Centeno; J. A. Odriozola. Hydrogen production by methanol steam

reforming on NiSn/MgO-Al₂O₃ catalysts: The role of MgO addition. *Appl Catal A* 2011;392:184–191.

[9] E. Nikolla, J. Schwank, S. Linic. Comparative study of the kinetics of methane steam reforming on supported Ni and Sn/Ni alloy catalysts: The impact of the formation of Ni alloy on chemistry. *J Catal* 2009;263:220–227.

[10] S. Saadi, B. Hinnemann, S. Helveg, C. C. Appel, F. Abild-Pedersen, J. K. Nørskov. First-principle investigations of the Ni₃Sn alloy at steam reforming conditions. *Surf Sci* 2009;603:762–770.

[11] M. Q. Fan, Y. Xu, J. Sakurai, M. Demura, T. Hirano, Y. Teraoka, A. Yoshigoe. Catalytic performance of Ni₃Sn and Ni₃Sn₂ for hydrogen production from methanol decomposition. *Catal Lett* 2014;144:843–849.

[12] M. Q. Fan, Y. Xu, J. Sakurai, M. Demura, T. Hirano, Y. Teraoka, A. Yoshigoe. Spontaneous activation behavior of Ni₃Sn, an intermetallic catalyst, for hydrogen production via methanol decomposition. *Int J Hydrogen Energy*, in press.

[13] J. H. Jang, Y. Xu, D. H. Chun, M. Demura, T. Hirano. Catalytic activity improvement of Ni₃Al foils for methanol decomposition by oxidation-reduction pretreatment. *Appl Catal A: Gen* 2011;398:161–167.

[14] W. S. Dong, H. S. Roh, Z. W. Liu, K. W. Jun, S. E. Park. Hydrogen production from methane reforming reaction over Ni/MgO catalyst. *Bull Korean Chem Soc* 2001;22:1323–1327.

[15] J. S. Lee, J. Kim, M. Kang. Hydrogen production from ethanol steam reforming over SnO₂-K₂O/Zeolite Y Catalyst. *Bull Korean Chem Soc* 2011;32:1912–1920.

Captions List

Table 1 BET surface areas (m^2/g) of Ni_3Sn after oxidation.

Table 2 BET surface areas (m^2/g) of Ni_3Sn after isothermal test or oxidation-reduction treatment.

Figure 1 Methanol conversion changed with methanol decomposition temperature for Ni_3Sn before (a) and after oxidation at 1073 K (b) and 1373 K (c).

Figure 2 Production rates of various gases changed with methanol decomposition temperature or Ni_3Sn before (a) and after oxidation at 1073 K (b) and 1373 K (c).

Figure 3 Methanol conversion changed with methanol decomposition temperature for oxidized Ni_3Sn before and after reduction at 603 K and 773 K. Ni_3Sn was oxidized at 1373 K.

Figure 4 Methanol conversion as a function of time on the stream at 713 K for Ni_3Sn (a) and at 603 K for Ni_3Sn after oxidation-reduction (b). The treated sample was Ni_3Sn oxidized at 1373 K and reduced for 1 h at 603 K.

Figure 5 TPR profiles for Ni_3Sn after oxidation at 1073 K and 1373 K.

Figure 6 XRD patterns for Ni_3Sn before (a) and after oxidation at 1073 K (b) and 1373 K (c).

Figure 7 SEM images of Ni_3Sn before (a) and after oxidation at 1073 K (b) and 1373 K (c).

Figure 8 XRD patterns for Ni_3Sn (a) and Ni_3Sn oxidized at 1373 K (b) and after reduction for 1 h at 603 K (c) and 773 K (d).

Figure 9 SEM images for Ni_3Sn oxidized at 1373 K (a) then reduced for 1 h at 603 K (b) and 773 K (c).

Figure 10 XRD patterns for Ni_3Sn before (a) and after the isothermal test (b) at 603 K.

Ni_3Sn was oxidized at 1373 K for 5 h and then reduced for 1 h at 603 K.

Figure 11 SEM images for Ni_3Sn after the isothermal test at 603 K. Ni_3Sn was oxidized at 1373 K for 5 h and then reduced for 1 h at 603 K.

Table 1

Oxidation temperature (K)	Surface area of Ni ₃ Sn alloy (m ² /g)
1373	0.5
1073	0.2
Without oxidation	0.1

Table 2

Ni ₃ Sn oxidized at 1373 K for 5 h	Surface area of Ni ₃ Sn alloy (m ² /g)
Without reduction	0.5
Isothermal test of 28 h at 603 K without reduction	0.5
Reduction for 1 h at 603 K	1.1
Reduction for 1 h at 773 K	0.9

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Sample	Element (At%)
a	C, 15.9; O, 50.3; Sn, 9.9; Ni, 23.9 Total, 100
b	C, 13.7; O, 20.2; Sn, 16.5; Ni, 49.6 Total, 100
c	C, 13.5; O, 9.9; Sn, 19.1; Ni, 57.5 Total, 100

Figure 10

Figure 11