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Novel highly active Ni–Re super-alloy nanowire type catalysts for CO-free hydrogen generation from steam methane reforming

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Abstract. Novel Ni–Re super-alloy nanowire type catalyst system is found for hydrogen generation from steam methane reforming. The novel nanowire type catalysts exhibit the super-high catalytic activity for hydrogen generation from steam methane reforming with CO-free in the product at lower reaction temperatures. The Ni–Re alloy nanowire type catalysts are active for converting methane and water to hydrogen and carbon dioxide at a low reaction temperature of about 623 K, which is about 200 K lower than that is needed for steam methane reforming on the conventional catalysts. The CO-free hydrogen is efficiently generated from steam methane reforming on the nanowire type catalysts at the lower reaction temperatures, in which water–gas shift reaction step is not needed for CO-free hydrogen production.

Keywords. Super-alloy nanowire type catalysts; low temperature H_2 generation from H_2O and CH_4; Ni–Re alloy nanowires.

1. Introduction

Hydrogen is not only an important green energy carrier, but also one of the main feedstocks for chemical industry production. Every year, about 53 million metric tons of hydrogen were consumed worldwide. There are no natural hydrogen deposits, and for this reason, the production of hydrogen plays a key role in modern society. The majority of hydrogen (∼95%) is produced from fossil fuels by steam methane reforming or partial oxidation of methane and gasification of coal, and only a small quantity by other routes, such as biomass gasification or electrolysis of water. For this process, two steps are needed, the first step is steam (H_2O) reacts with methane (CH_4) at high temperatures to yield syngas and water–gas shift reaction of CO with H_2O to yield CO_2 and H_2 in the second step. In our previous studies, Ni–Re alloy nanoparticles supported alumina as catalysts for steam reforming of methane and other hydrocarbons have been studied [1–7]. In the present presentation, Ni–Re alloy nanowires are used as the novel catalyst materials for steam methane reforming to generate hydrogen.

2. Experimental

The catalytic tests were carried out at lower reaction temperatures and at atmospheric pressure for steam reforming of methane in a fixed bed continuous-flow quartz reactor. Before the steam reforming reaction, the catalysts were reduced by H_2/N_2 at 703 K for 1 h. The nanowires type catalysts were characterized by XRD, SEM, etc. The metallic Ni nanowires and Ni–Re alloy nanowires are the products of Shokubai Wang Institute [8]. Figure 1 is the SEM image of the Ni nanowires synthesized by the Shokubai Wang Institute.

The Ni–Re alloy nanowires were prepared consequently by impregnating the Ni nanowires with aqueous solutions of $Ni(NO_3)_2$ and NH_4ReO_4 at room temperature, followed by drying, calcination and reduction with H_2. We can see from figure 1 that the size of the metallic Ni nanowires is homogeneously distributed and the average diameter of the nanowires is about 30 nm with the average length of about several micrometres.

3. Results

Figure 2 shows the XRD patterns of Ni–Re binary alloy and Ni–Re–Ce ternary alloy nanowires compared with that of Ni metallic nanowires. It is clear by comparing the XRD patterns of Ni–Re and Ni–Re–Ce alloy nanowires with that of Ni metallic nanowires in figure 2 that the 2θ angle of Ni (111), Ni (200) and Ni (220) peaks are shifted to the smaller 2θ angle after alloying Ni with Re.

Therefore, the XRD data in figure 2 are directly approved, the formation of Ni–Re nanoalloy by allowing Ni nanowires with Re.

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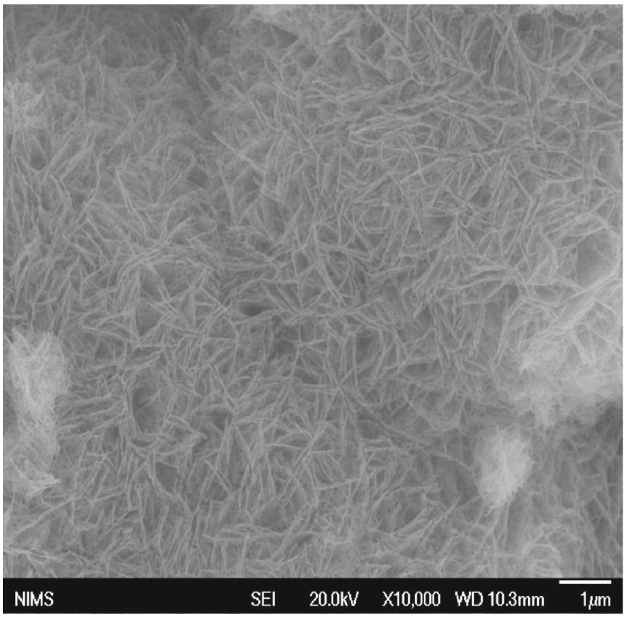

Figure 1. SEM image of Ni-based nanowires provided by Shokubai Wang Institute.

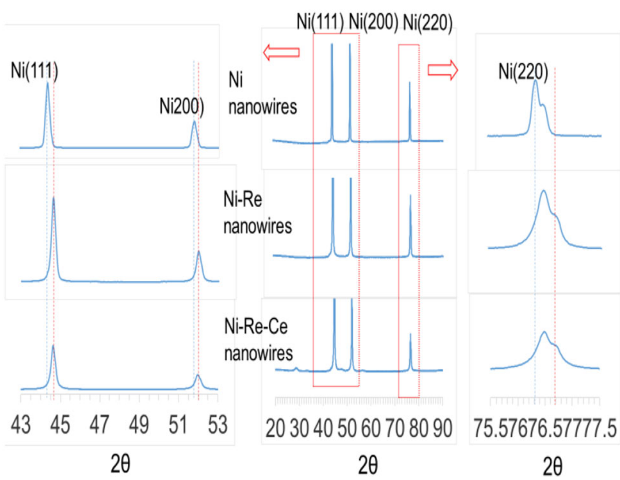

Figure 2. XRD patterns of Ni–Re alloy nanowires compared with that of pure Ni nanowires.

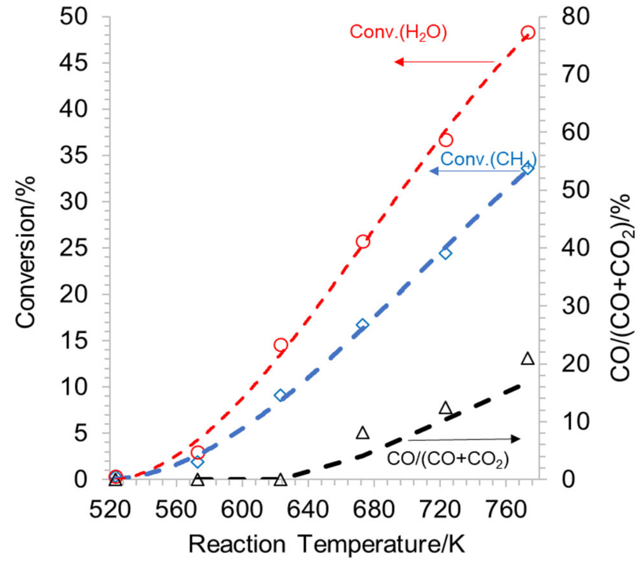

Figure 3. Conversions of methane and water and the mole ratio of CO/(CO + CO_2) in product for steam methane reforming on Ni–Re alloy nanowire type catalyst at the reaction temperature range of 523–773 K.

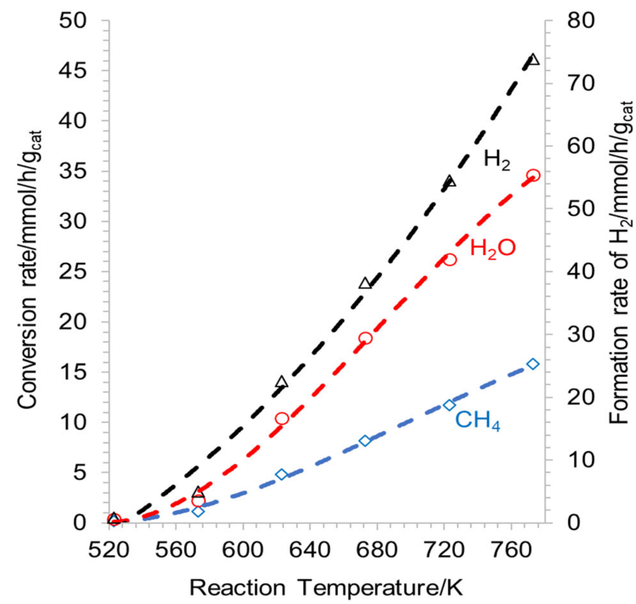

Figure 4. Formation rate of hydrogen and conversion rates of methane and water as a function of reaction temperature for steam methane reforming on Ni–Re/Ni nanowire type catalyst.

Figure 3 shows the catalytic performance of the Ni–Re alloy nanowire type catalyst for steam methane reforming to generate hydrogen as a function of reaction temperatures. We can see from figure 3 that the starting temperature for the reaction of methane with H_2O to generate hydrogen is about 523 K and the conversions of methane and water are increased with increasing reaction temperature. The product is composed of H_2 and CO_2 at the reaction temperature range of 523–623 K. The starting temperature for appearance of CO product is >623 K. The CO/(CO + CO_2) is increased gradually with increasing the reaction temperature from 623 to 773 K as shown in figure 3. Lower reaction temperatures are not thermodynamically favourable for the steam methane reforming at high conversions of methane and water. However, according to our previous achievements [9], high conversions are possible at the lower reaction temperature of <623 K can be expected if a Pd-based membrane reactor is used.

Figure 4 shows the conversion rates of methane and water with time on stream for steam methane reforming on Ni–Re alloy nanowire type catalyst at the reaction temperature range of 523–773 K.

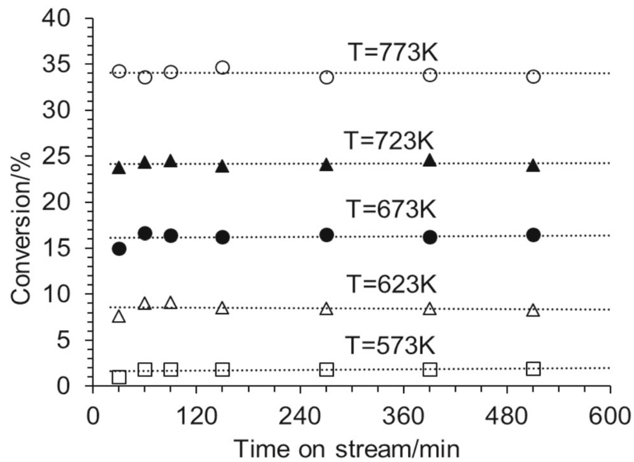

Figure 5. Conversions of methane with time on stream for steam methane reforming on Ni–Re alloy nanowire type catalyst at the reaction temperature range of 523–773 K.

Figure 5 shows the conversion rates of methane and water with time on stream for steam methane reforming on Ni–Re alloy nanowire type catalyst at the reaction temperature range of 523–773 K. We can see from figure 4 that a methane conversion rate of about 5 mmol $h^{-1}g_{cat}^{-1}$ and a water conversion rate of about 10 mmol $h^{-1}g_{cat}^{-1}$ are obtained for steam methane reforming to generate hydrogen and CO_2. The formation rate of CO-free hydrogen is about 20 mmol h^{-1} g_{cat}^{-1} at the low reaction temperature of 623 K.

4. Conclusion

Ni–Re alloy nanowires as a novel catalyst system exhibits the super-high catalytic activity for steam methane reforming to generate CO-free hydrogen at a lower reaction temperature of 623 K, which is about 200 K lower than that is needed for steam methane reforming on the conventional catalysts. The CO-free hydrogen is efficiently generated from steam methane reforming on the nanowire type catalyst at the lower reaction temperatures, in which water–gas shift reaction step is not needed for CO-free hydrogen production.

References

[1] Wang L, Murata K and Inaba M 2004 *Appl. Catal. A Gen.* **257** 43
[2] Wang L, Murata K and Inaba M 2004 *Appl. Catal. B Environ.* **48** 243
[3] Murata K, Wang L, Saito M, Inaba M, Takahara I and Mimura N 2004 *Energy Fuels* **18** 122
[4] Wang L, Murata K and Inaba M 2004 *Ind. Eng. Chem. Res.* **43** 3228
[5] Wang L, Murata K and Inaba M 2005 *J. Power Sour.* **145** 707
[6] Wang L, Murata K, Matsumura Y and Inaba M 2006 *Energy Fuels* **20** 1377
[7] Wang L, Murata K and Inaba M 2009 *Appl. Catal. A Gen.* **358** 264
[8] Wang L 2018 *J. Nanomed. Res.* **7** 200
[9] Wang L, Murata K, Sayari A and Grandjean B 2001 *ChemComm.* 1952