Designing Rooted Ni#Y_2O_3 Catalyst for Low-temperature Dry Reforming of Methane

Xiaobo Peng,[a] **Shusaku Shoji,**[b] **Masahiro Miyauchi,**[b] **Takeshi Fujita,**[c] **Hideki Abe**[a,*]
[a] *National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki, 305-0044, Japan.*
[b] *Department of Metallurgy and Ceramics Science, Graduate School of Science and Engineering, Tokyo Institute of Technology, Tokyo, 152-8552, Japan.*
[c] *WPI Advanced Institute for Materials Research, Tohoku University, Sendai, 980-8577, Japan.*
**E-mail address: abe.hideki@nims.go.jp*

Abstract: Low-temperature dry reforming of methane (LT-DRM) has always been a great challenge. Herein, we report an innovative way for the catalyst preparation, which combined a simple arc torch treatment with the subsequent calcination, was used in this LT-DRM process. By controlling the alloy precursors and calcination atmospheres, we designed a new rooted catalyst system; moreover, the rooted catalyst Ni#Y_2O_3 exhibited the excellent reactivity and long-term stability.

Keywords: Arc torch treatment, Rooted catalyst, LT-DRM.

1. Introduction (11-point boldface)

Dry reforming of methane (DRM: $CH_4 + CO_2 = 2CO + 2H_2$) presents a promising solution to convert CO_2 and CH_4 to subsequent chemical products[1]. However, due to the extreme inertness of CO_2 and CH_4, the reactant activation has always been a considerable challenge. To activate these reactants, the high reaction temperature was utilized, but the catalysts always suffered from active phase agglomeration and sintering[2]. Another key issue is the severe carbon deposition in the DRM process. CH_4 decomposition ($CH_4 = C(s) + 2H_2$) and CO disproportionation ($2CO = C(s) + CO_2$) resulted rapidly in carbon deposition and catalyst deactivation[3]. To further overcome these problems, we present a novel catalyst preparation method via arc torch treatment coupled with subsequent calcination for LT-DRM process. A new rooted catalyst system was designed. The rooted catalyst Ni#Y_2O_3, which consisted of the rooted nano-phase Ni and a Y_2O_3 matrix, possessed an excellent stability over more than 100 hours; moreover, the roots can tightly anchor the active phase and significantly enhance the reoxidation ability to resist the carbon accumulation.

2. Experimental

The nanophase-separated NiY with different atomic ratio were synthesized by using an arc torch method. Typically, the elemental metals of Ni and Y were added into the arc furnace. After the treatment of arc torch, the NiY particles were ground and sieved to obtain powder samples with an average size of 50 μm. The powder was further pretreated by the gas mixture of $CO/O_2/Ar$ or $CH_4/CO_2/Ar$. Then we obtained the samples with different structure and morphology. LT-DRM reaction was performed on a fixed-bed flow reactor operated at atmospheric pressure. In short, the catalyst (0.1g) was loaded in the quartz reactor (inner diameter = 10 mm). Then a gas mixture of $CH_4/CO_2/Ar$ with flow rate of 100 ml/min was introduced into the reactor. The temperature was raised to the desired reaction temperature (typically 723 K) to start the reaction. The reaction effluents were analyzed using the TCD of a gas chromatography equipped with an activated charcoal column. The catalytic performance after 6 h was typically used for discussion.

3. Results and discussion

As shown in Fig. 1, first we synthesized the NiY alloy precursor from the metal ingots of Ni and Y by using the arc torch treatment; moreover, the different alloy precursors (such as Ni_5Y, Ni_3Y, Ni_2Y, NiY and NiY_3) can be obtained via modulating the atom ratio of Ni and Y. Then the calcination process was employed to produce stable catalysts from the alloy precursor of NiY. The different calcination atmospheres can tune the location distribution between active phase and Y_2O_3 matrix. Through our exploration, the calcination atmosphere of CH_4/CO_2 mixture produced a core-shell catalyst of Ni#$Y_2O_3^{MCD}$ with the active phase coated by the Y_2O_3 matrix. Most importantly, the CO/O_2 atmosphere generated another kind of rooted catalyst of Ni#Y_2O_3 with the active phase sprouting from the Y_2O_3 matrix.

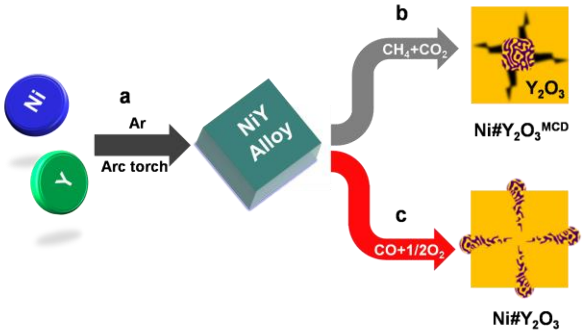

Figure 1. Scheme for the rooted catalyst preparation. (a) Transformation of metal Ni and Y into NiY alloy via the arc torch treatment ; (**b**) The preparation of Ni#$Y_2O_3^{MCD}$ over the mixture gas of $CH_4/CO_2/Ar$; (**c**) The preparation of Ni#Y_2O_3 over the mixture gas of $CO/O_2/Ar$.

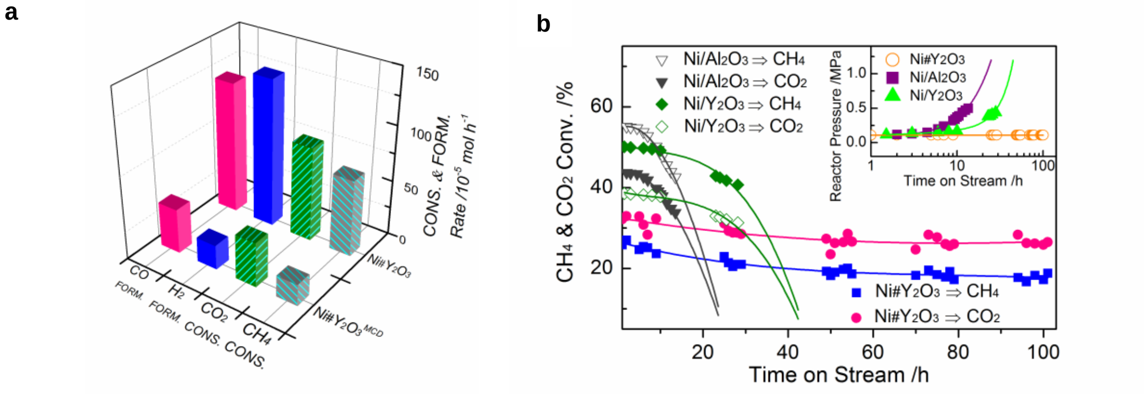

Figure 2. Catalytic results for various catalysts. (a) The LT-DRM performance over the Ni#Y_2O_3 and Ni#$Y_2O_3^{MCD}$. The consumption rate and formation rate was denoted as CONS. and FORM., respectively. (**b**) Stability of the Ni#Y_2O_3 and traditional supported catalysts in the LT-DRM.

The Ni#$Y_2O_3^{MCD}$ and Ni#Y_2O_3 were used for the LT-DRM reaction. The catalytic results are shown in Fig. 2a. The Ni#Y_2O_3 exhibited higher consumption rate to CH_4 and CO_2; moreover, the formation rate of H_2 and CO was also 6 times and 3 times higher than that of Ni#$Y_2O_3^{MCD}$, respectively. In addition, we further compared the Ni#Y_2O_3 with traditional supported catalysts for the durability of LT-DRM, as shown in Fig. 2b. The Ni#Y_2O_3 catalyst diaplayed a excellent stability for conversion of CH_4 and CO_2 over more than 100 hours. In contrast, the Ni/Al_2O_3 and Ni/Y_2O_3 showed rapid deactivation in a short period of time.

4. Conclusions

In conclusion, we designed a new catalyst preparation method, that is employing arc torch treatment to couple with the subsequent calcination. By tuning the alloy precursors and the calcination atmospheres, we successfully built a new rooted catalyst system for the LT-DRM process. The rooted Ni#Y_2O_3 exhibited higher LT-DRM reactivity than the other typical catalysts; moreover, it also possessed an excellent stability over more than 100 hours. The present work provides novel insights into low-temperature DRM process, and also offers entirely new preparation way and structure design to develop new catalytic materials.

References

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