Development and application of high performance Ni catalyst using heat-resistant γ-alumina

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Abstract: Ni-La reforming catalyst was improved by using heat resistant γ-alumina as carrier. The stability and activity of the catalyst at low S/C were comparable to Ru catalyst and retained high C_3H_8 conversion. The anti-coking ability was much better than the commercial Ni catalyst. Therefore, the development of high-performance Ni catalyst as a substitute for Ru catalyst will lead to the improvement of energy efficiency of entire hydrogen production process as well as the downsizing and cost reduction of the unit. Its wide range of application to fuel cell, hydrogen station and large-scale hydrogen production plant is expected.

Keywords: Hydrogen production, Reforming catalyst, Fuel cell.

1. Introduction

In comparison with the Ni based reforming catalysts, Ru catalysts have features such as:

① Easy to handle and no need of hydrogen reduction
② High activity
② Less coking and can be used on severe reaction conditions

and have been used on special case of high severe operating conditions as high-performance reforming catalysts in the field of chemical and city gas production. Recently, since it has been adopted as the reforming catalyst for fuel cell which requires both high performance and long life of catalysts, the consumption is increasing rapidly along with the spread of household fuel cell. However, as the amount of Ru resource is limited, securing of the resource and price change are big problems. In the field of fuel cell, because of the constraint of limited resource of Ru, it is necessary to develop substitute for Ru catalyst as soon as possible. Therefore, development of novel reforming catalysts with performance comparable to Ru catalyst by improving Ni based catalysts greatly contributes to the cost reduction and also the alleviation of its limited amount of resource, and this will accelerate the commercial application and spread of fuel cells.

2. Experimental

Ni-La catalysts were prepared by supporting La, an excellent co-catalyst, on heat-resistant γ-alumina, and the composition was optimized (Ni-La catalyst A). The catalyst B was obtained by adding a special co-catalyst to the catalyst A and modifying the preparation method. These catalysts were tested for 1000 h continuously using C_3H_8 as reforming gas at S/C=2.0, SV=60,000 and 450°C. The flow rates of C_3H_8, N_2, H_2 and H_2O were 60, 60, 6 and 360ml/min, respectively.

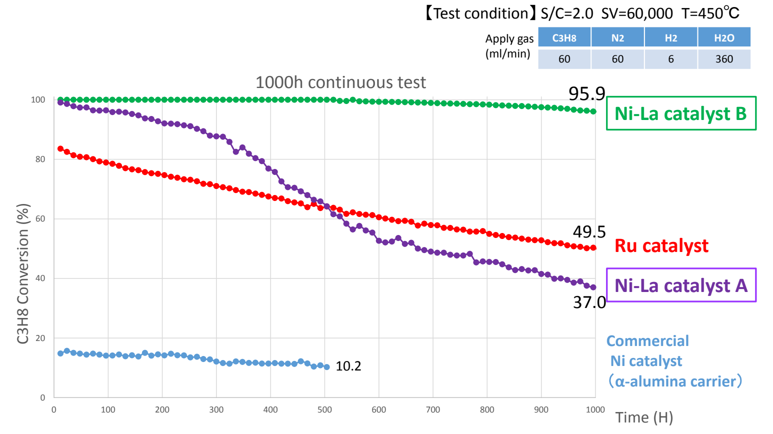

Figure 1. Time-course of C_3H_8 conversion in 1000 h continuous test.

3. Results and discussion

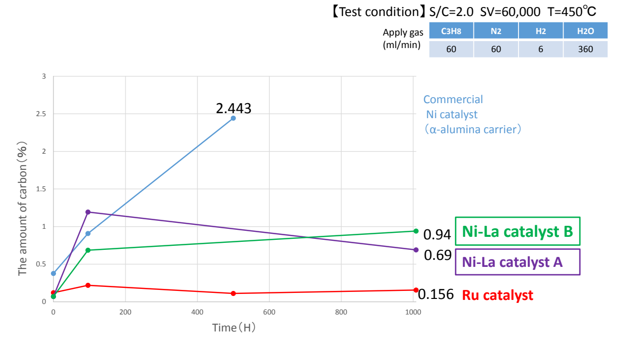

Figure 2. Amount of coking in 96 h and in 1000 h continuous tests.

When commercial Ni catalyst was tested, the pressure drop increased rapidly due to the clogging of the catalyst bed by formed carbon after 500 h. Figure 1 shows the time-course of C_3H_8 conversion for four catalysts during continuous experiments. Both the catalysts A and B showed very high conversion at the start of experiment. However, while the C_3H_8 conversion by catalyst A showed some fluctuation and decreased steadily, the catalyst B, which contained a special co-catalyst, retained high activity. The catalyst B was found to be very stable with very slow deactivation rate and the C_3H_8 conversion after 1000 h was as high as 95.9 %, which is 1.9 times that by the Ru catalyst.

Figure 2 compares the coking (amount of formed carbon) of four catalysts at 96 h and 1000 h after the start of continuous experiments. It is seen that the developed catalysts keep higher anti-coking performance and higher stability than the commercial Ni catalyst. The amount of coking observed after 1000 h continuous test were as follows. Ru catalyst: about 0.16%, catalyst A: 0.69%, 4.4 times that of Ru catalyst, catalyst B: 0.94%, 6.0 times that of Ru. These are about 15～20% of the coking amount of the commercial Ni catalyst tested for 500 h. The developed catalysts A and B produced very small amount of coking and kept high durability under the condition of low S/C (2.0) for about 1000 h.

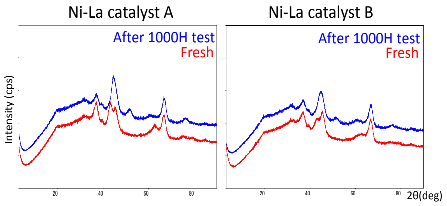

Figure 3. XRD results of catalysts A and B.

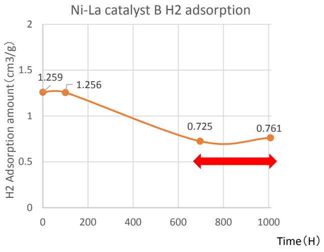

Figure 4. Amount of H_2 adsorption on catalyst B.

Further, the catalysts A and B before and after 1000 h test were analyzed on XRD to confirm the stability of the carrier. It is seen in Figure 3 that the crystal structure of carrier in the catalysts A and B is very stable and do not show significant degradation although slight changes are verified.

In addition, the amount of H_2 adsorption on catalyst B was measured after every continuous experiment to check the change in the active metal surface area. As shown in Figure 4, the amounts of H_2 adsorption after 700 h and 1000 h were almost the same, indicating that catalyst B did not degrade any more after 700 h and was very stable. As described above, the amount of coking of catalysts A and B were 4 - 6 times that of that for Ru catalyst. However, the amounts of coking per unit metal mass for catalyst A and B were lower than that of the Ru catalyst and 30 - 40 % lower than that for the commercial Ni catalyst. Therefore, both catalyst A and B developed in this study were confirmed to have extremely high anti-coking property.

4. Conclusions

We successfully developed the Ni-La catalyst by using heat-resistant γ-alumina as carrier. The catalyst performance was comparable to the Ru catalyst and showed high stability, high activity and high anti-coking performance in long-term continuous tests. The developed Ni-La catalyst are promising substitute for the Ru catalyst and are expected to be used in many field such as fuel cell, hydrogen station and large-scale hydrogen production.

Acknowledgements

The authors gratefully acknowledge funding for this work, which was provided by New Energy and Industrial Technology Development Organization (NEDO) and Japan Science and Technology Agency (JST). We wish to thank the help given by National Institute of Advanced Industrial Science and Technology (AIST), NICHe Tohoku University, IWAO JIKI KOGYO CO.,LTD.