

# Development of a new Synthesis Gas Production Catalyst and Process with CO<sub>2</sub> and H<sub>2</sub>O Reforming

Tomoyuki Mikuriya, Fuyuki Yagi and Mitsunori Shimura

## 1. Introduction

Production of synthesis gas from natural gas and conversion of synthesis gas to fuels and chemicals would become increasingly attractive due to the viewpoint for energy resource diversification and raising the price of crude oil. And the technology of synthesis gas production by reforming of natural gas with CO<sub>2</sub> and H<sub>2</sub>O is one of the effective solutions for the issues of energy resource and environmental preservation.

We have been investigating a new synthesis gas production catalyst and process with CO<sub>2</sub> and H<sub>2</sub>O reforming of natural gas. In this process, synthesis gases of various molar ratios of hydrogen to carbon monoxide are produced with high energy efficiency and low amount of carbon dioxide emission. Because the proprietary reforming catalyst with high resistance against carbon deposition could allow carbon dioxide and steam reforming reaction under optimal operation conditions with low carbon dioxide and steam to feed gas ratio.

In this paper, the characteristics and performance of the catalyst are introduced. And also the process study results of GTL, oxo-alcohol and acetic acid production with our synthesis gas production process are represented.

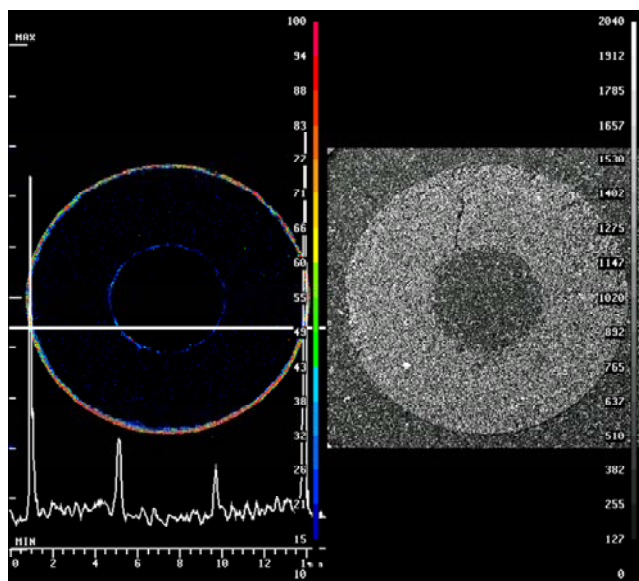
## 2. Characteristics and performance of the catalyst

The activity and stability of group VIII metal supported catalysts for CO<sub>2</sub> and H<sub>2</sub>O reforming depend crucially on both the metal and the support. It has been suggested that noble metals are less active for carbon formation than Ni and the carbon deposition is suppressed when the metal is supported on a metal oxide with strong Lewis basicity.<sup>1,2)</sup> Metal crystal structure and metal-support interaction may also be important to design the catalysts with the high resistance for carbon formation.<sup>3)</sup> Based on these considerations, we have designed a new noble metal supported catalyst for CO<sub>2</sub> and H<sub>2</sub>O reforming.

Fig.1 shows a result of EPMA(Electron Probe Micro Analyzer) analysis on our commercial size catalyst. The 4 peaks in left side figure indicate the concentration distribution of noble metal in the catalyst. Noble metal was loaded selectively on the outer surface of catalyst supports in egg-shell shape. As shown in this figure, metal content of inside is extremely lower than that of

outside. It is considered the effectiveness factor of reforming catalyst is less than 0.1, therefore, metals on the outer surface can only contribute to reforming reaction. So in our catalyst high price noble metal is effectively utilized with consideration for characteristics of reforming reaction.

Fig.1 Result of EPMA Analysis of the Catalyst

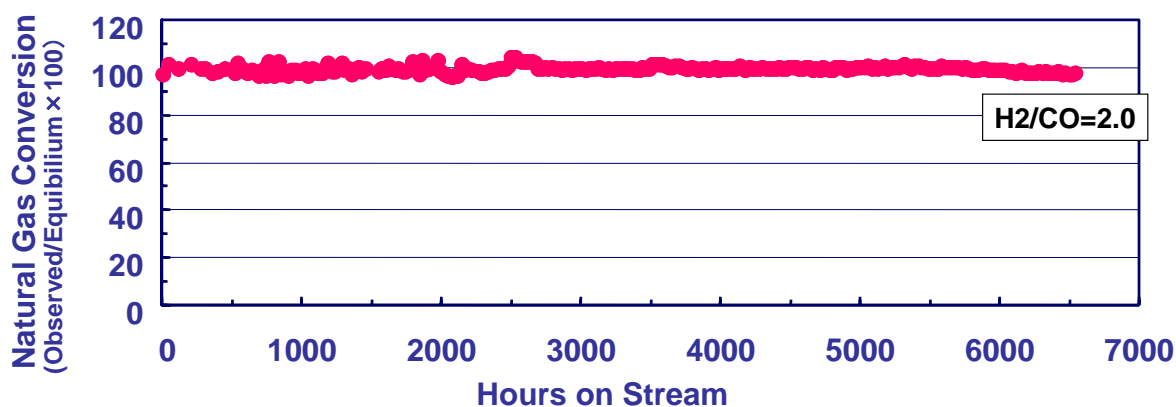


The pilot plant test of our CO<sub>2</sub> and H<sub>2</sub>O reforming catalyst was conducted. The mono tube reformer whose size is inner diameter of 110mm and length of 12m was applied for syngas production with hydrogen to carbon monoxide ratio of 2.0. This tube size is almost same as the commercial reformer tube. Around one hundred liter of the reforming catalyst were charged in the reformer tube. Design temperature and pressure are 1025°C and 2.4MPaG, respectively. Average syngas production rate is around 400Nm<sup>3</sup>/hr. Feed natural gas contains around 85% of methane and the rest are almost higher hydrocarbon than methane. This natural gas is reformed by the steam and carbon dioxide in the mono tube reformer without pre-reforming in this pilot plant.

Fig.2 presents pilot plant test results. At the start up condition, low pressure and high steam to carbon and carbon dioxide to carbon ratio was taken. In the normal operation condition, the temperature of catalyst bed outlet was set around 900°C. Operation pressure was 1.9MPaG. And ratios of carbon dioxide to carbon and steam to carbon of the feed stream were controlled to 0.4 and 1.15

respectively. As shown in this figure, the stable operation for around 7,000 hours has been confirmed under the target reaction condition. After the operation, catalyst was discharged and analyzed. The amounts of the carbon deposition on the catalysts were less than 0.1wt% in the each part of the catalyst beds. From the results, the carbon-free operation has been demonstrated.

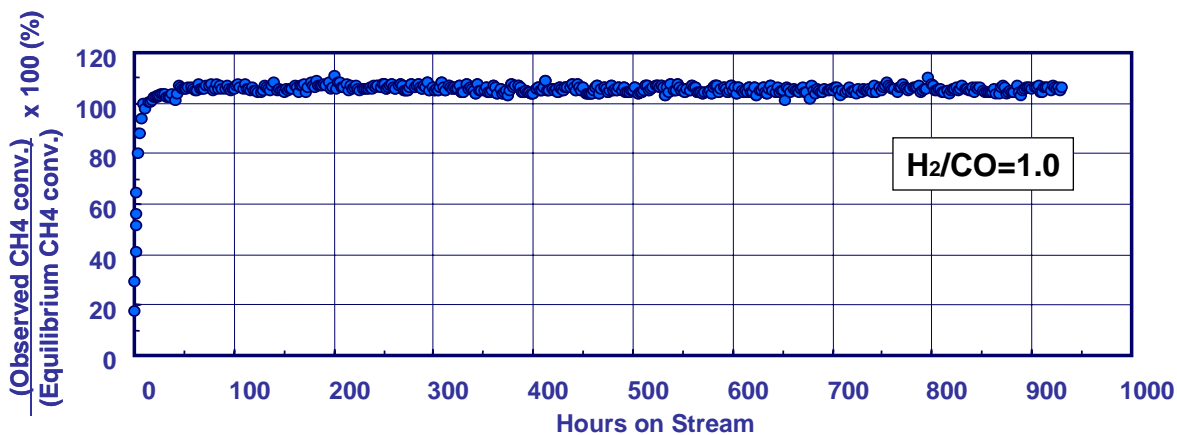
Fig.2 Pilot Plant Test Result of CO<sub>2</sub> and H<sub>2</sub>O Reforming Catalyst



Temperature (Catalyst bed outlet) : 865~895°C, Pressure : 1.5~1.9MPaG  
 Feed Molar Ratio Hydrocarbon/CO<sub>2</sub>/H<sub>2</sub>O = 1.0/0.4~0.6/1.15~1.64

Fig.3 shows the results of catalyst performance test in the Lab. scale for production of syngas with ratio of 1.0. Typical reaction conditions are as follows; Temperature of 850 °C ,Pressure : 2.0MPaG, Feed Molar Ratio Hydrocarbon/CO<sub>2</sub>/H<sub>2</sub>O/H<sub>2</sub> = 1.0/1.07/0.51/0.04. The 30cc of 3mm pellet catalyst were charged in the reactor. Long-run test for the production of syngas with low H<sub>2</sub>/CO ratio was attained around 1000hrs without catalyst deactivation.

Fig.3 Lab. Test Results the Catalyst for synthesis gas production of H<sub>2</sub>/CO=2.0



#### 4. Application studies of new synthesis gas production process for GTL, Oxo-alcohol (n-Butanol) and acetic acid synthesis

It is considered our synthesis gas production process makes superior economic sense when the carbon dioxide is available with low cost. In the Southeast Asia and Oceania, a lot of gas fields containing a large amount of carbon dioxide are found. In these natural gas fields, our process will be successfully applied to the syngas production as feed for FT oil, DME production.

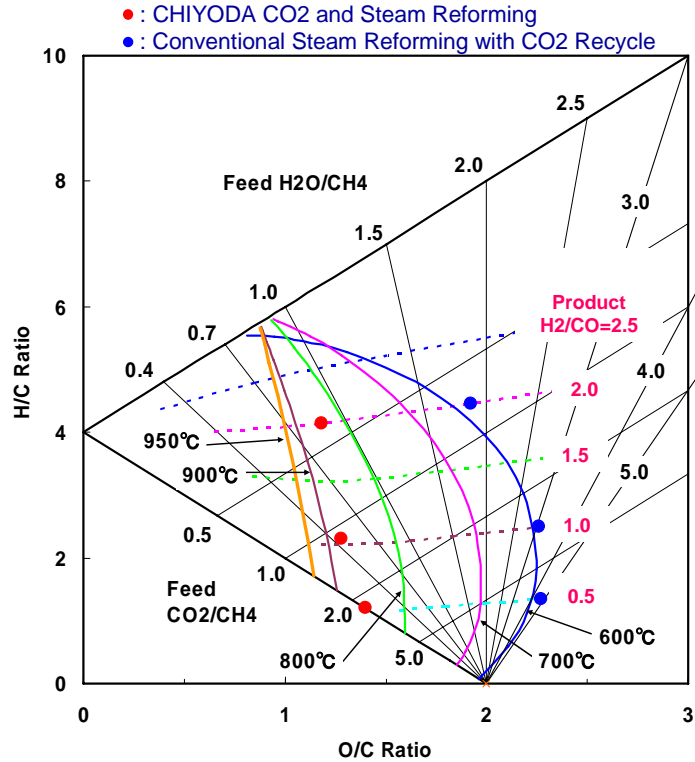
Another advantage of our process is represented in the application to GTL process integrated with LNG plants. A considerable amount of carbon dioxide is being exhausted in atmosphere form LNG plants. These carbon dioxides can be effectively utilized as a reforming agent for our process.

Our technology can also use the carbon dioxide which were exhausted from some kind of chemical plants, for example, ammonia plant and ethylene oxide as a raw material. These carbon dioxides are effectively utilized as reforming agent to produce synthesis gases for production of chemicals.

Application studies of our synthesis gas production process for GTL, Oxo-alcohol (n-butanol) and acetic acid synthesis processes were conducted in comparison with the conventional steam reforming process with CO<sub>2</sub> recycle. The plant capacities of GTL, n-butanol and acetic acid synthesis processes are assumed 10,000BPSD, 150,000ton/year and 500,000ton/year, respectively.

Feed gas conditions of our synthesis gas production process and conventional ones are represented on the carbon limit diagram<sup>4)</sup> in Fig.4. In this figure, the solid line connecting y-axis of 4.0 and x-axis of 2.0 represents the CO<sub>2</sub> to CH<sub>4</sub> molar ratio of feed gas and the straight line increasing from y-axis of 4.0 represents H<sub>2</sub>O to CH<sub>4</sub> molar ratio of feed gas. The product H<sub>2</sub>/CO molar ratios are presented dotted line in this figure. They are calculated the equilibrium gas compositions at the reformer outlet conditions of 950°C and 1.5MPa. For Fischer-Tropsch, n-butanol and acetic acid synthesis, the H<sub>2</sub>/CO molar ratio of product synthesis gases are taken 2.0, 1.0 and 0.5 respectively. It is obvious that operations on the left side of the carbon limit curve are more economical conditions because lower steam and carbon dioxide addition in feed to produce the synthesis gas for a given H<sub>2</sub>/CO ratio. But in these conditions, product synthesis gases have high thermodynamic potential for carbon formation. In our process, feed gas conditions on the left side of carbon limit line could be selected because our catalyst has high resistance against carbon formation.

**Fig.4 Feed Gas Conditions for Process Studies**

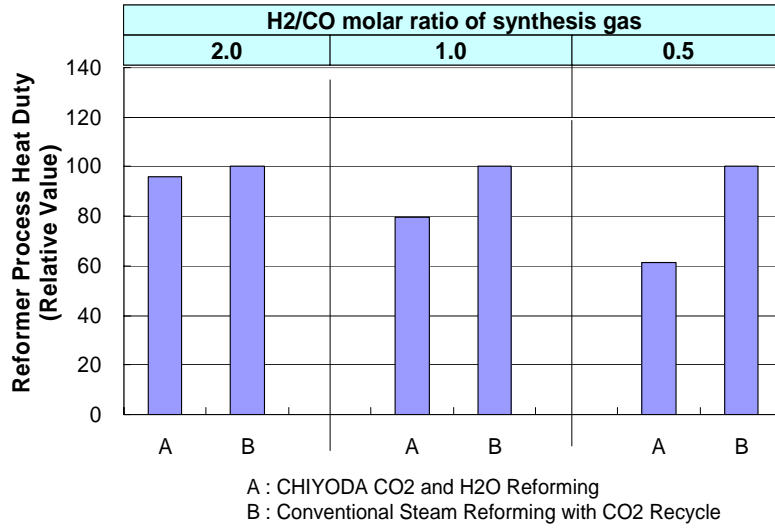


In the process studies, the configuration of synthesis gas production process is assumed as followed. The carbon dioxide in the product synthesis gas is separated by amine absorption and recycled to the feed stream. On the production of carbon monoxide for acetic acid synthesis, at first the synthesis gas with H<sub>2</sub>/CO molar ratio of 0.5 is produced by the reformer and then hydrogen is separated by PSA from the synthesis gas.

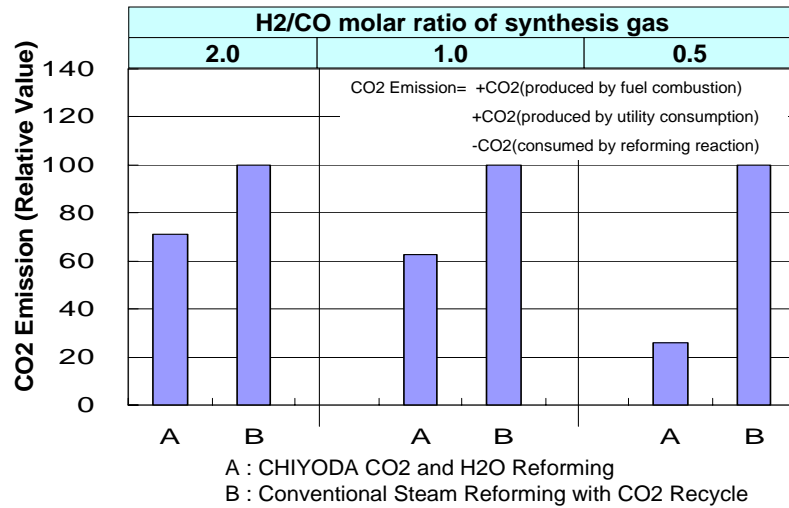
The typical study results are represented in Fig.5, 6 and 7. In these figures, all study results of our synthesis production process represented the relative values to the conventional ones at the same H<sub>2</sub>/CO molar ratios of synthesis gases.

Figure 5 shows the heat duty of reformer. Our reforming process represents the superior process efficiency because the fuel consumptions in the reformer are reduced in proportion to the reduction of process duty. For the case of synthesis gas production with lower H<sub>2</sub>/CO molar ratios, the difference of heat duties between our process and conventional one becomes larger. Because larger amount of carbon dioxide and steam addition in the feed stream is required for the conventional reforming process to avoid carbon formation on the catalyst.

**Fig.5 Estimated Heat Duty of Reformer**



**Fig.6 Estimation for amount of CO<sub>2</sub> Emission from Synthesis Gas Production Section**



**Fig.7 Plant Cost for Synthesis Gas Production Section**

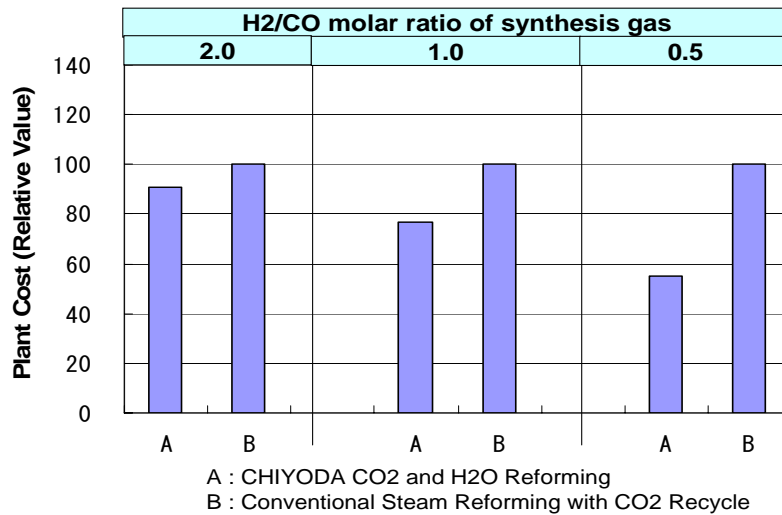


Fig.6 represents the estimated amount of carbon dioxide emission from synthesis gas production processes. The carbon dioxides produced by fuel combustion, steam generation in utility facility and consumed by reforming reaction are considered to calculate carbon dioxide emissions. Our reforming process can largely reduce the amount of carbon dioxide emission by 30~70% in comparison with conventional one. Because our process is superior to conventional one in fuel and utility consumption, especially in energy consumptions for excess CO<sub>2</sub> removal and recycle.

Fig.7 presents the estimated plant cost for synthesis production section. Main criteria and assumptions adopted for the economic analysis are summarized as follows;

- Assumed as Grass roots plant located in Middle East.
- Capital cost includes one-time catalyst charge cost.
- Feed : Natural Gas (0.75US\$/MMBTU) is assumed as representative of gas cost in Middle East.
- Feed CO<sub>2</sub> Gas : zero cost value
- On Stream Factor : 90% (8,000 h/year)
- Depreciation : 10% of total plant cost per year
- ROI before Taxes : 15% of total plant cost per year
- Tax and Insurance : 1% of total plant cost per year
- Maintenance cost : 3% of total plant cost per year
- Site preparation / piling / sewer / road / paving, 2-year spare parts, license fee & royalty, allowances & contingency, company overheads & profits are not included into the capital cost.

As shown in the figure, our processes represent superior economic sense to the conventional ones. This tendency became remarkable for the production of synthesis gas with lower H<sub>2</sub>/CO molar ratio.

##### 5. Further development of our synthesis gas production catalyst and process

Now we have been developing these catalyst and process in JOGMEC National GTL project. The GTL demonstration plant which has the synthesis oil production capacity of 500BPSD has been constructed in Japan. The demonstration test will be commenced in 2009.

## 6. References

- 1) J.R.Rostrup-Nielsen and J.-H. Bak Hansen, *J.Catal.*, 144, 38 (1993)
- 2) Z.L.Zhang and X.E.Verykios, *Catal.Today*, 21, 589 (1994)
- 3) M.C.J.Bradford and M.A.Vannice, *Catal.Rev.Sci.Eng.*, 41, 1 (1999)
- 4) N.R.Udengaard, J.-H. Bak Hansen and D.C.Hanson, *Oil & Gas J.*, Mar.9 (1992)