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Catalysis Today 104 (2005) 2–6
CATALYSIS TODAY
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Development of synthesis gas production catalyst and process

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Available online 18 April 2005

Abstract

The CO_2 reforming catalyst and process have been developed. The commercial size CO_2 reforming catalyst has been demonstrating its activity and stability in the gas to liquid (GTL) pilot plant tests for around 6000 h, and the first GTL oil from natural gas in Japan has been being produced from November 2002 to October 2004. In these tests, synthesis gas was generated by CO_2 and H_2O reforming with low CO_2/carbon and low H_2O/carbon ratios in feed gas composition. The proprietary catalyst which has high resistance against carbon deposition could allow the stable operation under CO_2 and H_2O reforming conditions. The CO_2 reforming simulator could well represent the results of the pilot plant tests. The proposed process showed superior economics on the feasibility studies of applications to GTL processes.

Keywords: CO_2 reforming; Catalyst; GTL; Pilot plant; Simulator; Economics

1. Introduction

Recently, GTL processes are greatly paid attention as effective technologies for utilization of natural gas fields on middle or small scales, which are not economical for LNG production [1–4]. In these processes, the capital cost of synthesis gas production section is considered to account for around 60% of the total capital cost [3,4]. Therefore, the development of more compact syngas production processes with high-energy efficiency has been expected.

New CO_2 reforming catalyst and process have been developed on GTL national project by Japan Oil, Gas and Metals National Corporation (JOGMEC) since 1999. The process can directly generate the stoichiometrically balanced synthesis gases which have excess of neither H_2 nor CO as suitable feed gases for Fisher–Tropsch (FT) synthesis, methanol and dimethyl ether and so forth. In this process, natural gas is reformed in a tubular reformer with CO_2 and H_2O as reforming agents so an expensive oxygen plant is not needed.

The proprietary catalyst with high resistance against carbon deposition can produce synthesis gases by lower CO_2/carbon and H_2O/carbon molar ratios in the feed gas composition with low energy consumption. The pilot plant tests of this process were successfully carried out at Yufutsu gas field in Japan (Fig. 1).

2. Experimental

Accelerated catalysts life tests (dry reforming) were employed to develop the commercial catalyst in bench scales. The commercial ring catalysts of 16 mm outer diameter, 8 mm inner diameter and 16 mm length were prepared by loading of novel metals on metal oxide supports. An average side crushing strength of the catalysts was 500 N/piece. These catalysts were crushed into 2–4 mm size, and 50 cc of them were loaded to the reactor. The reaction tests were carried out with feed CO_2/CH_4 ratio of 1.0, the reaction conditions at 850 °C, 2.0 MPa G and GHSV = 6000 1/HR. Under the dry reforming conditions, especially at high pressure, the product synthesis gases have high thermodynamic potential for carbon formation. Nielsen et al. defined the carbon activity as the indication of carbon formation possibility [5–7]. If this value exceeds to 1.0, carbon will deposit. Under our dry reforming condition, the carbon activity at the bottom of the catalyst bed was 2.6.

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0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.03.061

Fig. 1. Overview of JOGMEC GTL pilot plant (7 barrels per day).

For the pilot plant operations, about 120 L of commercial catalysts were charged in mono-tube reformer that tube has 12.0 m length and 11.0 cm inner diameter, and were reduced with hydrogen at around 800 °C under atmospheric pressure before starting the reaction tests. Natural gas was fed to the reactor with CO_2 and H_2O. Synthesis gas with $H_2/CO = 2$ was produced directly by CO_2 and H_2O reforming of natural gas. H_2O/CO_2/carbon ratio of feed gas was 1.15–1.64/0.40–0.60/1.00 and reaction conditions were 865–890 °C, 1.5–1.9 MPa G at the outlet of the reactor and GHSV was 3000 1/HR. Natural gas composition, $C_1/C_2/C_3/C_4/C_5/C_6/N_2$, was 85.8/8.3/3.1/1.3/0.1/0.1/1.3 vol%, respectively, and total sulfur content was around 1 ppm.

3. Results and discussion

The typical results of the dry reforming are shown in Fig. 2. A conventional steam reforming catalyst was deactivated immediately under this condition. The newly developed CO_2 reforming catalyst could maintain a stable activity for about 300 h. Carbon deposition occurs extremely easily from produced synthesis gas in equilibrium state at high pressure such as 2.0 MPa G. Continuous 300 h operation for CO_2 reforming, under this condition, has never been reported. These results supported the robustness of the catalyst against carbon deposition. After about 380 h on stream, the catalyst was treated under steam reforming, and it was confirmed that the catalyst could be regenerated. This result indicates that the morphology of carbon deposited on catalyst surface seems to be a material like an atomic carbon that is easily converted into carbon monoxide by steam. And we think steam plays a significant role to remove the carbon precursor from the catalyst surface, and beneficial in situ catalyst regeneration with steam is available.

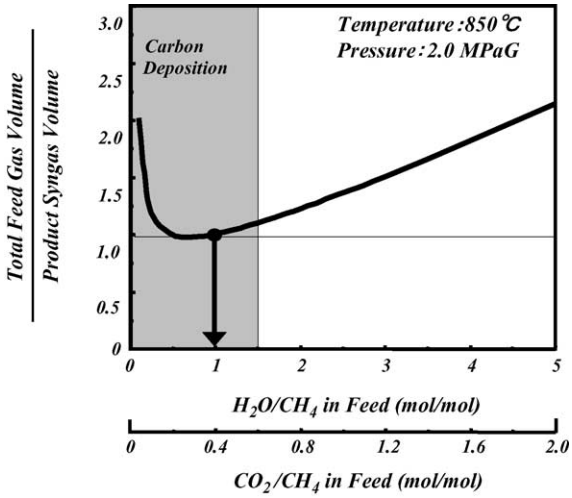

Fig. 3. Optimal CO_2/CH_4 and H_2O/CH_4. Molar ratio in feed gas to produce syngas ($H_2/CO = 2.0$) for FT synthesis.

Fig. 3 shows the relation between the feed gas composition and required feed gas volume to obtain the unit volume of synthesis gas having H_2/CO molar ratio of 2.0. The volumes of synthesis gases were estimated by the equilibrium calculation of steam reforming and water–gas shift reactions at 850 °C and 2.0 MPa G. At the point of nearby feed molar ratio of $CH_4:CO_2:H_2O = 1.0:0.4:1.0$, the feed gas volume is minimized and it is predicted that preferable operations with lower energy consumption can be accomplished. But in the case of CO_2 and H_2O reforming with conventional reforming catalysts, the selection of these operating conditions is prohibited by higher potential for carbon formation, and particular technologies for suppress of carbon deposition will be required [5–9,11–13,20].

The results of the pilot plant operation are shown in Fig. 4. In this figure, the conversions of natural gas are presented by comparison with the percentage of the equilibrium values at the same reaction conditions. The

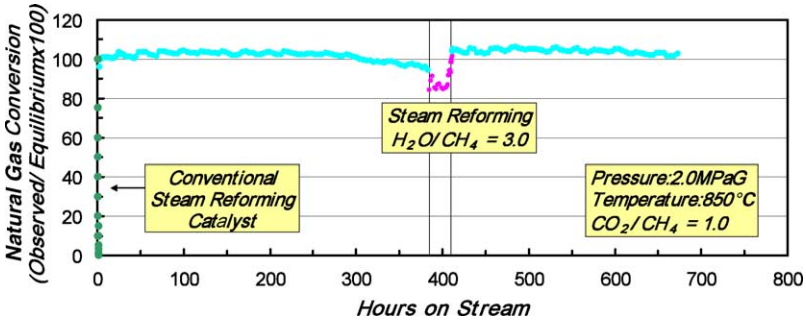

Fig. 2. Results of accelerated catalyst life tests.

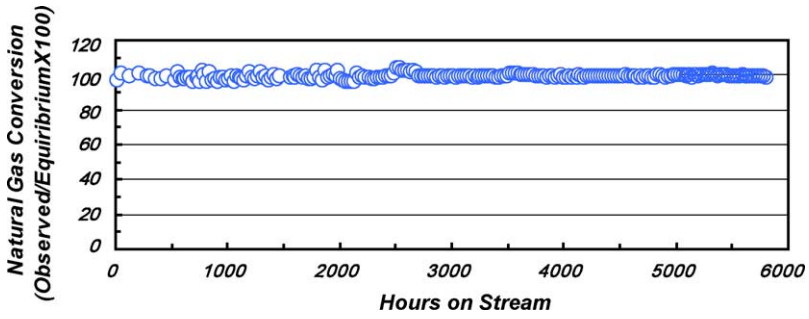

Fig. 4. Results of Pilot Plant Tests for H_2O/CO_2 reforming ($C_1/C_2/C_3/C_4/C_5/C_6/N_2$ = 85.8/8.3/3.1/1.3/0.1/0.1/1.3 vol%, H_2/CO = 2.0, H_2O/CO_2/carbon ratio = 1.15–1.64/0.40–0.60/1.00, 865–890 °C, 1.5–1.9 MPa G).

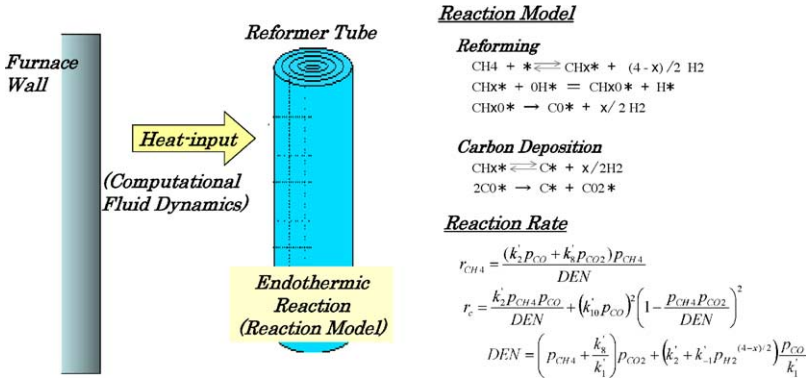

Fig. 5. CO_2 reforming simulator.

stable operation for 6000 h has been attained under around target reaction condition (H_2O/CO_2/carbon ratio = 1.15–1.64/0.40–0.60/1.00, 865–890 °C, 1.5–1.9 MPa G). H_2/CO ratio of product gas was adjusted to 2.0 in this test. During the operation, little change of the temperature and pressure drop of the catalyst bed was observed. After the tests, the catalyst was discharged from the reformer and the carbon content of the catalysts was determined. The amounts of the carbon deposition on the catalysts at the all positions in the reactor were less than 0.1 wt%. From these results, the carbon-free operation was successfully demonstrated.

The design concepts of our commercial size catalysts are described as follows. Based on several reports [11–15,17,22], we suppose reaction model of H_2O/CO_2 reforming. Methane is adsorbed on metal surface, and it is dehydrated into CH_x species [11–15]. Support is considered to take an important part for the activation of H_2O and CO_2 [11–15,22], especially at metal-support interface [11–13]. CH_x species is oxidized to CH_xO species, and this CH_xO species is decomposed to H_2 and CO [17]. This model is mainly referred to the paper reported by Bradford and Vanicce [17].

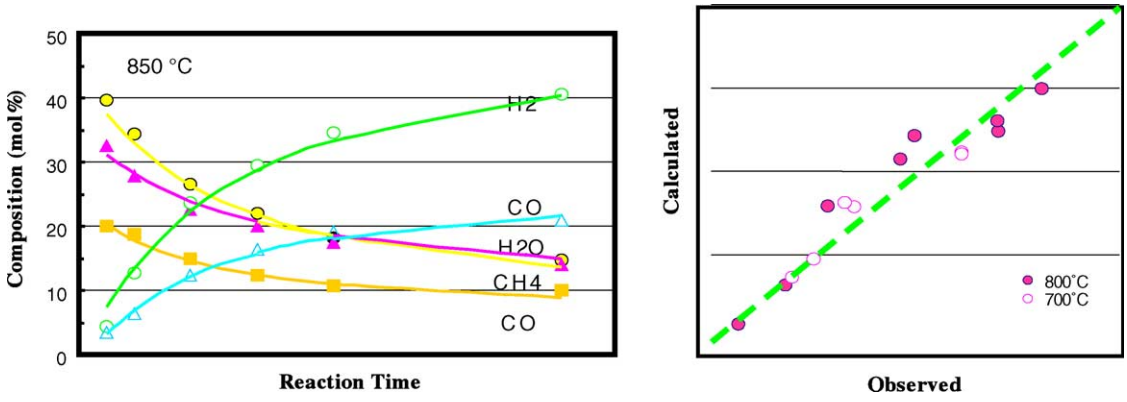

Fig. 6. Results of parameter fitting for reforming rate and carbon formation rate.

Deposited carbon could be originated from two types of precursors, CH_x (Dent reaction; Eq. (1)) and CO (Boudouard reaction; Eq. (2)).

$$CH_4 \leftrightarrows C + 2H_2 \quad (1)$$

$$2CO \leftrightarrows CO_2 + C \quad (2)$$

Simultaneous interception of both carbon deposition routs is required for CO_2 reforming catalyst. Basic support is considered to suppress carbon deposition originated from CH_x precursors [18,19]. As to suppress of Boudouard reaction, some explanations have been done [16,17,22]. Although basic support would be effective for the suppress of Dent reaction, excessive strong basicity seems to proceed Boudouard reaction, because CO_2 will be formed stably on the basic sites, and this reaction will proceed to carbon deposition. Noble metal would show high durability against carbon deposition because of low carbon solubility [7], and high metal dispersion and strong interaction between metal and support would be also required for suppress of carbon deposition [8,9,11–13,18,19,22]. Catalyst acidity is considered to be one of factors on carbon deposition under reforming conditions [10]. Giving thought to all above information, we have prepared proprietary CO_2 reforming catalyst by loading noble metal on support with desirable acidity and basicity [23–25].

The simulator to predict the temperature profile and gas compositions in the catalyst bed have also been developed for the design of the tubular reformer (Fig. 5). The heat-input to the reformer tube from the burners was calculated by computational fluid dynamics, and the endothermic heat-flux was calculated by the simulator. The modeling of reactions for reforming and carbon formation on the catalyst surface is conducted with consideration from the laboratory experimental results and information on literatures [17]. Our model is essentially same as the one proposed by Bradford and Vanicce [17]. Catalysts life under optional operation conditions can be estimated because the carbon formation rate is taken into the consideration. Representative elementary reactions are shown in Fig. 5. The reaction rate of CH_4 and the carbon formation reaction rate are expressed by the rate constant on elementary reactions and the partial gas pressures.

Typical fitting results to determine kinetics parameters are shown in Fig. 6. The left figure shows the result for reforming reaction rate. Changes of gas compositions according to the contact time are presented. The right figure shows the results for carbon deposition rate. Horizontal axis presents observed value and vertical axis shows calculated result. Parameter fitting was carried out at the same time for both reactions. The plots mean the observed value, and corresponding curves present the calculation results. As shown in these figure, calculation results represented observed value well, and thus kinetics parameters in reaction model could be obtained.

Typical simulation results of the pilot plant tests are shown in Fig. 7. This figure stands for the typical axial temperature profiles of the catalyst bed. The plots show the observed value, and corresponding curves present the calculation results. As shown in this figure, calculation results fitted with observed value well. The calculated gas composition of the reformer outlet also agreed with the observed values. Through the analysis of the pilot plant test results by the simulator, it was confirmed that it could be effectively used for the CO_2 reformer design.

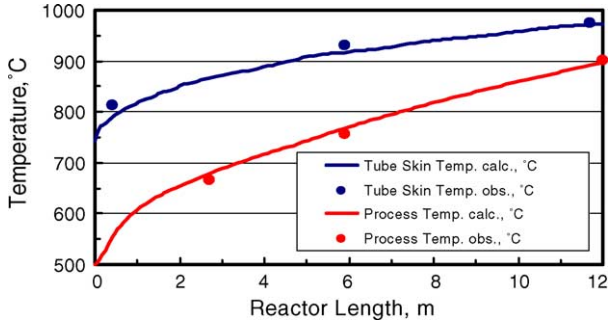

Fig. 7. Estimation of temperature profile in reformer.

The feasibility studies of the new GTL process for the utilization of the medium or small size of natural gas fields in the Southeast Asia have been done in the GTL national project program. Almost 85% number of natural gas fields in the world is medium or small sizes. Especially in the Southeast Asia, a lot of those medium or small gas fields containing a certain amount of CO_2 are found. In those natural gas fields, the CO_2 reforming process will be successfully applied to the synthesis gas production as feed for FT synthesis. The basic assumptions of the feasibility studies are as follows. Gas field size; 1.75TCF, plant capacity; 15,000 barrels per day (stand alone/grass roots), natural gas composition; $CH_4/C_2H_6/C_3H_8/C_4^+/N_2/CO_2 = 77.5/1.0/0.3/0.3/0.8/20.1$ (vol%). As the result of the studies, it is estimated that the plant cost is US$ 460 million, and the product oil price is around US$ 25/barrel.

Another advantage of the CO_2 reforming process is represented in the application to GTL process integrated with LNG plants. A considerable amount of CO_2 is being exhausted in atmosphere form LNG plants. That CO_2 can be effectively utilized as a reforming agent in the process and, it is also possible to share utility and offsite supplementary facilities with LNG plant. For example, a natural gas field containing 3.5 vol% of CO_2 can be utilized to GTL process of 15000BPSD size. With combination of LNG and GTL plants, more than US$ 1.4/barrel of cost reduction is expected on with the stand-alone case.

4. Conclusion

The activity and stability of the CO_2 reforming catalyst has been substantiated through the pilot-scale operation. We will finish this pilot plant test at the end of October 2004. With the successful completion of this test, we would like to

make the catalyst and process promising candidates for utilization of the middle or small scale of natural gas fields.

Acknowledgement

Grateful acknowledgements for the financial support are made to Japan Oil, Gas and Metals National Corporation.

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