Hydrogen production technology development using coke oven gas (COG)

Kenji Nakao,[a,]* **Mamoru Kasugai,**[a] **Kimihito Suzuki,**[a] **Nobuaki Ito,**[a] **Hitoshi Dohnomae** [a]

[a] *Nippon Steel and Sumitomo Metal Corporation, 20-1 Shintomi, Futtsu, Chiba 293-8511, Japan*

**Corresponding author: (Fax) +81 439 80 2745, (E-mail) nakao.6nz.kenji@jp.nssmc.com*

Abstract: The key technology for reducing CO_2 emission involves the catalytic reforming of higher hydrocarbons, e.g., coal tar in coke oven gas (COG), to lower hydrocarbons followed by steam reforming. Catalytic steam reforming of the coal tar in COG at ~1,073 K was performed using a NiMgO-based catalyst in a bench plant (BP2; 50 Nm^3-COG/h) equipped at Muroran Works. The catalyst showed very high activity and successfully achieved the hydrogen amplification ratio set in the project under severe conditions such as extremely high concentrations of hydrogen sulfide (ca. 0.2%–0.3%) and condensed aromatics, which easily cause coking.

Keywords: NiMgO, Steam reforming, Coke oven gas.

1. Introduction

In the carbonization of coal in the steel-making process, coke oven gas (COG) is emitted as a by-product of coke at a level of 300–350 Nm^3 per ton of coal. Crude COG mainly comprises hydrogen and methane and also includes a few percents of carbon monoxide, carbon dioxide, tar, and impurities such as hydrogen sulfide. Under a very high catalyst poisoning concentration of hydrogen sulfide in hot crude COG, such as 0.2%–0.3%, steam reforming of hydrocarbon compounds and the water-gas shift reaction using hot crude COG would be promising to amplify the amount of hydrogen in hot crude COG in spite of the high temperature (ca. 1073 K) of crude COG, which should easily facilitate thermal cracking and pyrolysis of aromatics. If catalytic reforming of hot crude COG becomes possible, it would greatly contribute to CO_2 reduction in the hydrogen-production process. Therefore, production of hydrogen directly from hot crude COG via catalytic reforming is of great significance.

In this research, we present a newly developed NiMgO based catalyst ($Ce/NiMgO+Al_2O_3$) prepared via a solid-phase crystallization process rather than the conventional process of impregnating the catalyst support with catalytic metal from the surface. The $Ce/NiMgO+Al_2O_3$ catalyst shows little coke formation and a high catalytic activity[1]. In the COURSE50 (CO_2 Ultimate Reduction in Steelmaking process by innovative technology for cool Earth 50) project[2], which has been ongoing since 2008 in Japan, technologies for reducing CO_2 emission from the steel-making process have been developed. One such technology includes partial reduction of iron ore in the blast furnace using hydrogen-amplified COG produced via catalytic reforming of hot crude COG. The key technology for reducing CO_2 emission is catalytic transformation of higher hydrocarbons, e.g., coal tar in crude hot COG, to lower ones followed by their steam reforming.

2. Experimental

The $Ce/NiMgO+Al_2O_3$ catalyst was prepared according to the procedure described in Ref.1. The molar ratio of Ni:Mg:Ce was 1:8:1, and the catalyst's outer diameter was 15 mm, inner diameter was 5 mm, and height was 15 mm. Catalytic steam reforming of the coal tar in hot crude COG at ~1,073 K was performed using the NiMgO based catalyst in BP2 at Muroran Works. Prior to catalytic reforming, the catalyst was pre-reduced with a H_2/N_2 (20/30 Nm^3/h) mixed gas at 1,023 K for 0.5 h. The flow rates of the hot crude COG introduced to the reformer were controlled at ~50 Nm^3/h using Ar as a tracer under monitoring using an online gas chromatograph (GC) equipped with a TCD. The reforming conditions were as follows: steam to carbon molar ratio (S/C) = 0.8 and space velocity (SV) = 500 h^{-1}. During burn-off, the deactivated catalyst was oxidized using ~50% air in the N_2 mixed gas (50 Nm^3/h). The gas compositions at both the inlet and outlet of the reformer were measured using an online TCD-GC. The catalytic activity was evaluated in terms of the hydrogen-amplification ratio, which is defined as the ratio of the H_2 volume in the reformed gas to that in hot crude COG, where each H_2 volume was calculated using H_2 concentration and the whole gas volume. The amounts of carbon and sulfur deposited on the spent catalyst were measured using a Carbon/Sulfur analyzer. The physicochemical properties of catalyst are characterized by XRD and XPS techniques.

3. Results and discussion

We built the BP2 at Muroran Works (Photograph 1). The BP2 is possible for long run test using COG and evaluation of the catalytic durability. Furthermore, it is aimed at evaluation of non-catalytic partial oxidation (POX) performance, especially, evaluation of performance of CH_4 decomposition and H_2 amplification. The target is H_2 amplification ratio of twice and long run test over 500 hours.

To investigate the evaluation of the catalyst stability, a repeated test for catalytic steam reforming of coal tar in COG and its regeneration was conducted in BP2. The hydrogen amplification ratio as a function of time on stream is shown in Figure 1. The semi-long run test for 100 hours was achieved by repeating catalytic reforming and its regeneration. Figure 2 shows the average hydrogen-amplification ratio in each reforming number. The amplification ratio was kept about 1.4 times after 4 times repeated. From Carbon/Sulfur analysis, there was no accumulation of carbon and sulfur on the catalyst after the test.

Photograph 1 Main appearance of BP2

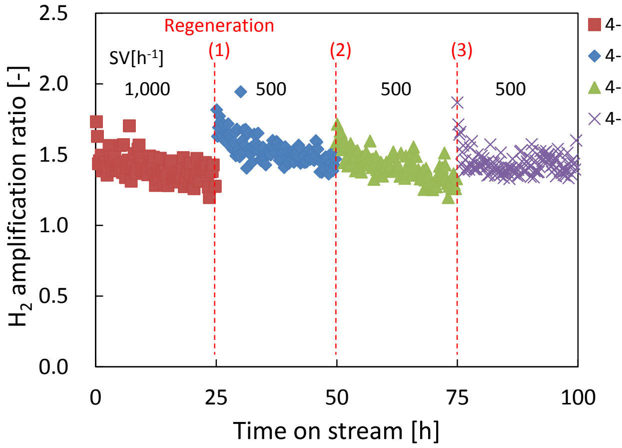

Figure 1. Time on stream of H_2 amplification ratio.

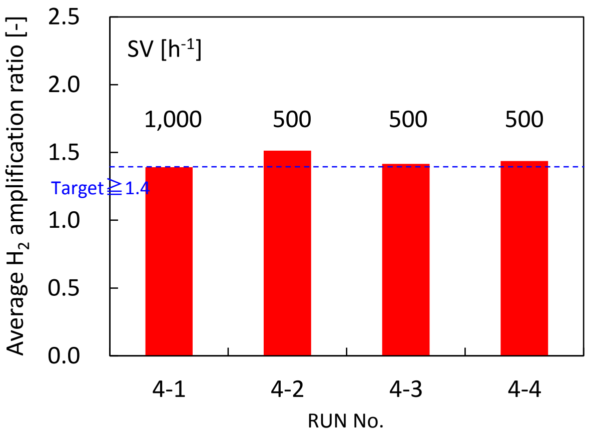

Figure 2. Average H_2 amplification ratio in the repeated test

COG 50 Nm^3/h, Steam/Carbon=0.8, SV=500, 1,000 h^{-1}, 1,073 K, 25 h

4. Conclusions

We developed the hydrogen production technology and clarified the mechanism of catalytic reaction. The semi-long run test for 100 h was achieved by repeating catalytic reforming and its regeneration in BP2. The hydrogen-amplification ratio was kept about 1.4 times even after 4 times repeated in BP2. There was no accumulation of carbon and sulfur on the catalyst after the test.

Acknowledgements

This article is based on results obtained from "Development of technologies for environmentally harmonized steelmaking process, 'COURSE50'" project commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

References

1. K. Suzuki and K. Fujimoto, PCT International Publication No. WO2010/134326 (2010).
2. URL : http://www.jisf.or.jp/course50/index_en.html