Pre-Combustion CO$_2$ Capture Using Ceramic Absorbent and Methane Steam Reforming

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A novel CO$_2$ separation technique that employs the chemical reaction of lithium-containing oxides with CO$_2$ has been developed. Since this method is effective in the temperature range of 450 °C to 700 °C, it has the advantages of enabling CO$_2$ separation in power plants without lowering the temperature and of absorbing CO$_2$ from the steam-methane reforming process at the same time. Because the absorption is exothermic and the steam reforming is endothermic, the energy loss is expected to be significantly reduced by combining the reactions. Hydrogen yields are expected to be higher because the equilibrium may be shifted by the removal of the CO$_2$ by-product. We have therefore proposed a pre-combustion CO$_2$ capture system using lithium silicate and steam reforming. Bench-scale experiments were performed to measure the methane conversion and CO$_2$ removal efficiency in order to evaluate the feasibility of the pre-combustion CO$_2$ capture system. At temperatures of less than 650 °C, the methane conversion in the case of mixture of catalyst and absorbent was higher than that in the case of catalyst alone. In addition, the CO$_2$ removal efficiency is almost 90%. These results appear to indicate that pre-combustion CO$_2$ capture combined with steam reforming is feasible.

[Received August 9, 2004; Accepted December 15, 2004]

Key-words : CO$_2$, Capture, Absorbent, Pre-combustion

1. Introduction

To reduce global warming, the reduction of carbon dioxide (CO$_2$) emissions is essential. Promising measures for this purpose include the saving of energy, the improvement of conversion efficiency, the development of alternative energy sources, and the separation of CO$_2$. Regarding the separation of CO$_2$, the removal of CO$_2$ from the high-temperature fuel gas of power plants is thought to be effective. However, most CO$_2$ removal techniques have poor heat tolerance. The authors have developed a novel CO$_2$ separation technique that employs the chemical reaction of lithium-containing oxides, such as Li$_2$ZrO$_3$ and Li$_2$SiO$_3$, with CO$_2$. Since this method is effective in the temperature range of 450 °C to 700 °C, it has the advantages of enabling CO$_2$ separation in power plants without lowering the temperature and of absorbing CO$_2$ from the steam-methane reforming process at the same time.

Since the absorption is exothermic and the steam reforming is endothermic, the energy loss is expected to be significantly reduced by combining the reactions. Hydrogen yields are expected to be higher because the equilibrium may be shifted by the removal of the CO$_2$ by-product. This process is known as the Sorption Enhanced Reaction Process and has been studied extensively around the world. In most cases, the CaO calcination reaction is used for CO$_2$ removal. However, the absorption properties are degraded due to the grain growth caused by cyclic use at the high CO$_2$ emission temperatures in this reaction. For lithium silicate on the other hand, the emission temperature is about 200 °C lower than that of CaO, and the degradation of the absorption properties is correspondingly small. We have therefore proposed a pre-combustion CO$_2$ capture system using lithium silicate and steam reforming.

Bench-scale experiments were performed to measure the CO$_2$ removal efficiency and methane conversion in order to evaluate the feasibility of the pre-combustion CO$_2$ capture system. In particular, we tried to confirm the Sorption Enhanced Reaction Process by CO$_2$ absorption.

2. Experimental procedures

Commercially available steam-reforming nickel catalyst (E51V-3, Nikki Universal Co., Ltd.) and lithium silicate as a CO$_2$ absorbent (LS-HE905, Toshiba Ceramics Co., Ltd.) were used for this bench scale test. This lithium silicate contains 2 mol% of potassium carbonate to promote CO$_2$ absorption as is the case of lithium zirconate. A mixture of steam-reforming catalyst and CO$_2$ absorbent was placed in a metal reactor that was 50 mm in diameter and 1200 mm in height. The reactor was heated externally. The gases were introduced from the top and removed from the bottom, and were changed by switching the valve settings. Figure 1 shows the temperature and gas profiles used in this bench-scale test. Initially, the reactor was heated to 150 °C. Next, H$_2$ was introduced to reduce the catalyst and to increase the temperature to 600 °C. After 30 min, H$_2$ was switched to N$_2$ and the temperature was increased to 700 °C. Then, N$_2$ was switched to CH$_4$ and steam to start the steam reforming process. With the progress of steam reforming, the temperature was gradually decreased to the range required for CO$_2$ absorption and was maintained at 600 °C for about 30 min. After that, CH$_4$ was stopped and the temperature was increased to 700 °C and maintained at this temperature for CO$_2$ emission. Finally, steam was switched to N$_2$ and the reactor was cooled to room temperature.

In this experiment, the pressure and space velocity were fixed at 200 kPa and 1625/h, respectively. In addition the weight ratio of catalyst to absorbent and flow rate of steam to carbon...
were also fixed at 1:4 and 4:1, respectively.

The CO\textsubscript{2} removal efficiency and CH\textsubscript{4} conversion were calculated from the change of flow rate between the inlet and outlet. The flow rate of each gas at the outlet was calculated from the total gas flow rate and the individual gas concentrations. The gas flow rate was measured using a wet-type gas flow meter (W-NK50, Shinagawa Co., Ltd.). The gas concentrations were measured using a micro gas chromatograph (CP 4900, GL Science Co., Ltd.).

3. Results and discussion

Figure 2 shows the temperature dependence of CH\textsubscript{4} conversion. At temperatures of more than 650°C, both in the case of mixture of catalyst and absorbent and catalyst alone, the CH\textsubscript{4} conversions were almost the same. However, at temperatures of less than 650°C, the CH\textsubscript{4} conversion in the case of mixture of catalyst and absorbent was higher than that in the case of catalyst alone. This result suggests that an enhanced reforming reaction occurs in this temperature range. Figure 3 shows the time dependence of CO\textsubscript{2} removal efficiency at 600°C. It was found that the CO\textsubscript{2} removal efficiency was kept at around 90% for up to 45 min. Therefore, the enhanced reforming reaction was thought to occur due to CO\textsubscript{2} absorption.

Figure 4 shows the cyclic behavior of methane conversion at 600°C. It was found that the methane conversion decreased gradually. However, the decrease was almost saturated after 8 cycles. On the other hand as shown in Fig. 5, CO\textsubscript{2} removal efficiency hardly changed up to 10 cycles. Therefore, it was thought that the decrease of CH\textsubscript{4} conversion was not due to the degradation of absorbent. When the CO\textsubscript{2} absorption occurred due to lithium silicate at temperatures of more than 500°C, eutectic molten carbonate composed of Li\textsubscript{2}CO\textsubscript{3} and K\textsubscript{2}CO\textsubscript{3} was formed\textsuperscript{2} and kept at the inner pores of absorbent. However, in the case of mixture of catalyst and absorbent, the molten carbonate seems to move into catalyst because of the capillary effect originating from the micropores. Then, the activity of catalyst is thought to decrease since the penetrated molten carbonate reacts with or covers the catalyst metal. In order to clarify the degradation mechanism of CH\textsubscript{4} conver-
sion, microstructure observation and compositional analysis of both the catalyst and absorbent used are needed.

4. Conclusion

The results of the experiments appear to indicate that pre-combustion CO$_2$ capture combined with steam reforming is feasible. To confirm that this system can actually be used in practice, experiments must be conducted over several hundreds of cycles to verify long-term stability. Research is under way to determine the best operating conditions for these experiments.

Acknowledgements This work was supported by the New Energy and Industrial Technology Development Organization (NEDO), Ministry of Economy, Trade and Industry Japan as a key technology research project.

References