Heating Effect of Plasma Catalytic Reaction on the CH_4 Reforming of CO_2 over Ni/γ-Al_2O_3 Catalyst in Dielectric-barrier Discharge Reactor

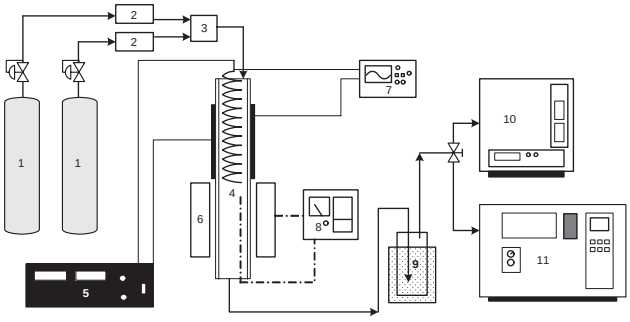
Hwaung Lee,[1] Hyung Keun Song,[1] and Byoung Ryul Min*[2]
[1]*Clean Technology Research Center, Korea Institute of Science and Technology, P. O. Box 131, Cheongryang, Seoul 136-791, Korea*
[2]*Department of Chemical Engineering, Yonsei University, 134 Shinchon-dong, Seodaemun-ku, Seoul 120-749, Korea*

(Received April 3, 2006; CL-060393; E-mail: hwaung@kist.re.kr)

CH_4 reforming of CO_2 reaction for producing synthesis gas (syngas) was performed using dielectric-barrier discharge (DBD) with catalyst. Ni/γ-Al_2O_3 was used as a catalyst. To investigate the effect of reaction temperature, extra heating was applied outside of the plasma reactor. When supplied extra heating, pure syngas could be obtained only at 573 K. It is a noticeable result comparing with pure catalytic reaction or plasma reaction only.

Methane is the major component of natural gas and one of the possible alternative energy sources. Among all greenhouse gases, however, methane with CO_2 also contributes the most of man-made greenhouse effect. Any successive process development of a feasible utilization of both CH_4 and CO_2 will signify the achievement of double objectives of slowing down a buildup greenhouse gases in the atmosphere and better carbon resource utilization. CH_4 reforming of CO_2 to syngas has recently attracted considerable interest as one method of solving this objective. This process is strongly endothermic reaction.[1–3] It could occurr at high temperature with proper catalyst. A desirable alternative is the plasma methane conversion. When using low temperature plasma, this reaction occurr at a low temperature because methyl radicals can be easily formed in the plasma. For plasma chemical reactions, free radicals are believed to be much more important than any other reactive particles. Therefore, control and manipulation of the subsequent free-radical reactions are essential to the success of plasma applications.[4] The electrons within the plasma serve principally to excite and decompose the gas molecules at a high rate and in a non-selective fashion. To overcome this difficulty, heterogeneous catalysts can be introduced into the plasma reaction. This catalysis-assisted plasma technology does not only enhance the decomposition efficiency catalytically, but also reduces the by-products selectively. For this reason, intensive efforts have been devoted to the plasma catalytic reaction.[5–12] However, plasma catalytic reaction is not the same as pure catalytic reaction, because the catalytic activity of most catalysts makes an appearance at high temperature. Typically, plasma process for chemical reaction is carried out at room temperature. Although the electron temperature of low temperature plasma is very high, the gas temperature is not. Low-temperature plasma cannot provide sufficient temperature for catalytic activity. In this study, to enhance the syngas selectivity, some extra heat was supplied into the plasma catalytic reactor.

The catalyst was prepared by incipient-wetness method. Aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ was impregnated on the support, γ-Al_2O_3. The catalyst dried at 393 K and then calcined in O_2 condition at 973 K for 2 h. The catalyst was reduced at 973 K in H_2 conditions for 2 h just before reaction. In all experiments, the Ni content of catalyst was fixed at 5 wt % and 1 g of catalyst was used in each experimental set. The BET surface area of prepared catalyst was 121 m^2/g after reduction. The experimental setup was shown schematically in Figure 1. The reactor was made of a long quartz tube. The length of reactor was 500 mm, and inner diameter was 6 mm. The upper part of outside wall of the reactor was coated with silver as a ground electrode. The length of electrode was 200 mm. The inner electrode was made of stainless steel spring having the outer diameter of 4 mm and located at the center of the reactor. The catalyst was packed in the lower part of plasma zone and electric furnace was installed on the catalyst. Detail reactor configuration was shown in Figure 2. The high-voltage generator applied 2.5 to 4.0 kV sinusoidal waveforms. The frequency was fixed at 20 kHz in all experimental sets. The thermocouple was set up under the catalyst bed to monitor the bulk gas temperature and control the furnace temperature. All the experiment was carried out at atmospheric pressure. The flow rates of feed gases, CH_4 and CO_2, were controlled with a mass flow controller. The total feed flow rate was fixed at 30 mL/min and the ratio of feed gases



1. Gas Cylinder (CH_4, CO_2) 2. Mass Flow Controller 3. Gas Mixture
4. Plasma Reactor 5. AC Power Supply 6. Furnace 7. Oscilloscope
8. Heat Controller 9. Cold Trap 10, 11. GC

Figure 1. A schematic diagram of experimental apparatus.

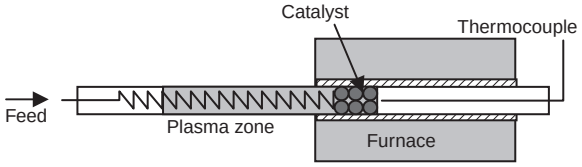


Figure 2. Reactor details.

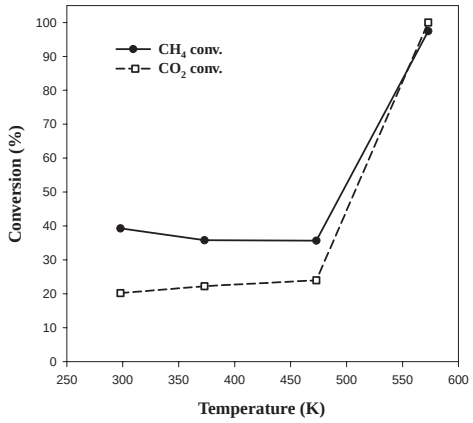


Figure 3. Effect of heating temperature on the conversion.

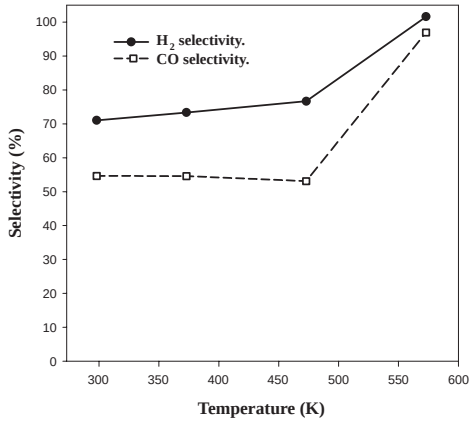


Figure 4. Effect of heating temperature on the selectivity.

(CH_4/CO_2) was 1. Qualitative and quantitative analysis of products were carried out on-line with two gas chromatographs.

As shown in the Figure 2, the plasma zone was partially overlapped with heating zone, and whole catalyst section was in the heating area. The length of catalyst bed was about 40 mm, so the furnace was covered with 45 mm of electrode for full coverage. Until the temperature approached up to 473 K, there was no change on the conversion of CH_4 and CO_2. However, the conversion of CH_4 and CO_2 was jumped up remarkably under the temperature of 573 K. Figures 3 and 4 showed the conversion of reactants and selectivity of syngas. When an input power was 80 W and the temperature of the heater was 573 K, the conversion of CH_4 was 97.45% and the conversion of CO_2 was almost 100%. Here, the selectivity of H_2 was almost 100% and the selectivity of CO was 96.92%. To compare with pure catalytic activity, the same experiments were performed without plasma. The result was shown in Figure 5. In this case, more than 1073 K was required to obtain 98% of CH_4 conversion and 100% CO_2 conversion. Both selectivities of CO and H_2 reached above 95% at 873 K or higher. This result shows that when plasma energy was supplied, the catalytic activity was carried out at lower temperature, in this case, as high as 500 K.

It is a noticeable result comparing with pure catalytic reaction or plasma reaction only. The conversion of CH_4 was 40% using DBD, and just 2% using catalyst. However, only

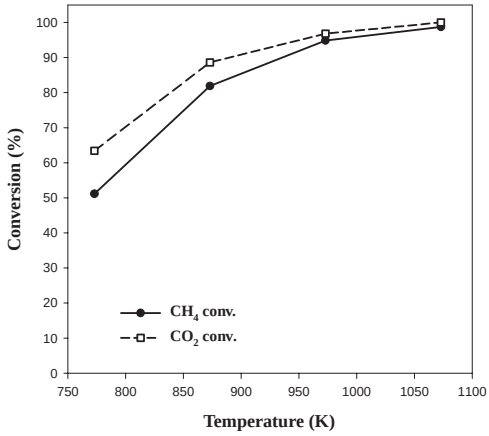


Figure 5. Pure catalytic reaction with Ni/Al_2O_3.

80 W of plasma energy was supplied, the reaction was fully performed at 573 K. This phenomenon was not appearing in any other different reactor layouts. If whole plasma reactor was covered with electric furnace, the reactor was broken due to the high temperature. If only catalyst part was covered with furnace, the conversion was not increasing at 573 K. Actually, temperature of catalyst bed in the reactor was increased more than setting temperature of the furnace. This synergetic effect made the conversion and selectivity so high. This system, combined with plasma and catalyst, could be suggested a new way to produce syngas effectively.

In addition, by measuring the consumed power, the plasma with catalyst system supplied additional heating at 573 K dissipated 126 W of power, but catalytic system without plasma used 155 W at 1073 K. Therefore, this system is very effective not only in reaction performance but also economical.

This work was supported by National Research Laboratory program of Korea Science and Engineering Foundation.

References

1 J. H. Edward, A. M. Maitra, *Fuel Process. Technol.* **1995**, *42*, 269.
2 I. Wender, *Fuel Process. Technol.* **1996**, *48*, 189.
3 C. H. Lin, J. X. Wang, J. H. Lunsford, *J. Catal.* **1988**, *111*, 302.
4 J. Huang, M. V. Badani, S. L. Suib, J. B. Harrison, M. J. Kablauoi, *Phys. Chem.* **1994**, *98*, 206.
5 T. Jiang, C.-J. Liu, G.-L. Fan, *Chem. Lett.* **2001**, 322.
6 S.-S. Kim, H. Lee, B.-K. Na, H. K. Song, *Catal. Today* **2004**, *89*, 193.
7 M. Heintze, M. Magureanu, *J. Catal.* **2002**, *206*, 91.
8 C.-J. Liu, K. Yu, Y.-P. Zhang, X. Zhu, F. He, B. Eliasson, *Appl. Catal., B* **2004**, *47*, 95.
9 Z.-H. Li, S.-X. Tian, H.-T. Wang, H.-B. Tian, *J. Mol. Catal.* **2004**, *211*, 149.
10 C.-J. Liu, R. Mallinson, L. Lobban, *Appl. Catal., A* **1999**, *178*, 17.
11 C.-J. Liu, B. Xue, B. Eliasson, F. He, Y. Li, G.-H. Xu, *Plasma Chem. Plasma Process.* **2001**, *21*, 301.
12 S.-S. Kim, J. S. Choi, J. S. Kim, H. Lee, H. K. Song, *J. Ind. Eng. Chem.* **2005**, *11*, 533.

Published on the web (Advance View) May 20, 2006; doi:10.1246/cl.2006.646