

Combination of Partial Oxidation and CO₂ Reforming of Methane over Monolithic Ni/CeO₂-ZrO₂/γ-Al₂O₃ Catalyst

Xuan LI, Yun TENG, Mao Chu GONG, Yao Qiang CHEN*

College of Chemistry, Sichun University, Chendu 610064

Abstract: A new monolithic Ni/ CeO₂-ZrO₂/γ-Al₂O₃ catalyst for combined partial oxidation and CO₂ reforming of methane was prepared. The result shows that the addition of O₂ to the feed can improve the activity of the catalyst and adjust the H₂/CO ratio of the productive gases.

Keywords: Partial oxidation, CO₂ reforming, methane, nickel catalyst.

Due to the growing concern about the effective utilization of natural gas, the conversion of natural gas into hydrogen and carbon monoxide (syngas) which may be used industrially for the synthesis of chemical products, such as hydrocarbons, oxygenated compounds, and polycarbonates, has received extensive attention in recent years¹. Traditionally, syngas has been produced by the steam reforming of methane (SRM). However, this reaction is highly endothermic and produces a syngas with an H₂/CO ratio higher than that required for the Fischer-Tropsch synthesis and for the production of methanol (H₂/CO=2)².

Partial oxidation of methane (POM) to syngas is a mildly exothermic reaction, which has high reaction rate and affords syngas with a H₂/CO ratio of about 2³, as CO₂ reforming with methane is a highly endothermic process and the yields syngas with H₂/CO ratio of ≤1⁴. They both are interesting alternative for the production of syngas. The combination of these two reaction can improve the reactor temperature control, reduce the formation of hot spots and make the process energy more efficient, besides allowing the production of syngas with a wider range of H₂/CO ratio (H₂/CO can be varied between 1 and 2 by manipulating the relative concentrations of O₂ and CO₂ in the feed)⁵.

Nickel based catalysts have shown an excellent behavior in the conversion of methane, with an activity comparable to noble metal catalysts⁶. It was also reported that CeO₂-ZrO₂ solid solution showed a high catalytic activity, particularly for oxidation of CH₄⁷. In this paper, a new monolithic Ni/ CeO₂-ZrO₂/γ-Al₂O₃ catalyst was prepared and used for combined partial oxidation and CO₂ reforming of methane.

The CeO₂-ZrO₂ mixed oxide was prepared by using a co-precipitation method. The CeO₂-ZrO₂ mixed oxide and a commercial γ-Al₂O₃ was impregnated separately with an aqueous solution of Ni(NO₃)₂, and then dried at 393 K for 2 h, calcined at 873 K for 2 h. The two kinds of powders were blended in ration of 1:9, and some water was added

* E-mail: nic7501@email.scu.edu.cn

into the mixture to ball milling. The resulting slurry was wash-coated onto a monolithic substrate, then dried at 393 K for 2 h and calcined at 873 K for 2 h. The catalyst contained 8wt% of nickel.

The combined partial oxidation and CO₂ reforming of methane reaction were performed at atmospheric pressure in a fixed-bed reactor. The feed gases consisted of CH₄, O₂ and CO₂. The catalytic reactions were conducted at 1123 K and a flow rate of 50 cm³/min. The product gases were analyzed by an on-line GC equipped with a TCD detector.

Partial oxidation of methane and CO₂ reforming of methane using different gas compositions over the monolithic Ni/CeO₂-ZrO₂/γ-Al₂O₃ catalyst were carried out, and the C:O ratio was held constant of 1. The effect of oxygen content on catalytic performance is shown in **Table 1**. When there was no O₂, CH₄ and CO₂ conversion were only 30.7% and 36.1% respectively. The addition of O₂ to the feed increased CH₄ and CO₂ conversion, this implies that O₂ is better than CO₂ in activating CH₄. When O₂ content reaches 25~30vol%, the catalyst shows good activity, CH₄, CO₂ conversion and H₂ selectivity are above 90%. The H₂/CO ratio of the products varied from 0.9 to 1.8 with increased amounts of O₂ in the feed stream. It is just one of the advantages of the combined reaction.

Table 1 The catalytic performance over 8wt% Ni/CeO₂-ZrO₂/γ-Al₂O₃ catalyst for combined partial oxidation of the methane and CO₂ reforming of the methane using feed with different compositions monolithic

O ₂ content (vol %)	X _{CH₄} (%)	X _{CO₂} (%)	S _{H₂} (%)	H ₂ /CO
0	30.7	36.1	94.2	0.9
5	47.2	44.8	93.7	1.1
10	59.0	51.8	93.2	1.2
15	70.3	65.5	92.6	1.3
20	85.8	86.4	95.7	1.4
25	90.6	93.5	97.0	1.6
30	94.4	93.8	98.2	1.8

Acknowledgments

The authors would like to thank the National Natural Science Foundation of China (No: 20273043) and the National Key Basic Research Project of China (G1999022407) for providing financial support for this project.

References

1. V. K. Venkataraman, H. D. Guthrie, *et al.*, *Stud. Surf. Sci. Catal.*, **1998**, 119, 913.
2. D. J. Wihelm, D. R. Simbek, A. D. Karp, *et al.*, *Fuel Process. Technol.*, **2001**, 71, 139.
3. K. Heitenes, S. Lindberg, O.A. Rokstad, A. Holmen, *Catal. Today*, **1995**, 24, 211.
4. J. R. Rostrup-Nielsen, J. H. Bak Hansen, *J. Catal.*, **1993**, 144, 38.
5. V. R. Choudhary, A. M. Rajput, B. Prabhakar, *Catal. Lett.*, **1995**, 32, 391.
6. Q. Miao, G. X. Xiong, S. S. Sheng, *et al.*, *Appl. Catal. A*, **1997**, 154, 17.
7. J. A. Montoya, E. Romero-Pascual, C. Gimón, *et al.*, *Catal. Today*, **2000**, 63, 71.

Received 9 May, 2004