Development of Carbon Free Catalysts for CO_2-CH_4 Reforming

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Introduction

The application of CO_2-CH_4 reforming technology in the conversion of biomass and landfill gases can generate "Green Power" and "Bio-Energy" fuels of hydrogen-rich gas for fuel cells [1]. At the same time it could significantly reduce the greenhouse gas emission. The synthesis gas produced through CO_2-CH_4 reforming is the desired feedstock for Firscher-Tropsch synthesis with a lower H_2/C ratio [2]. However, only a few processes using CO_2-CH_4 reforming have been commercialized (CALCOR process [3] and SPARG process [4]). The successful achievement of the economic and environmental benefits based on CO_2-CH_4 reforming is essentially dependent on the catalyst stability. From the industrial standpoint, it is more practical to develop non-noble metal catalysts due to the high cost of noble metals. Ni is the most often investigated non-noble metal. However, severe carbon formation limits the application of Ni-based catalysts.

A series of Ni-based dual active component catalysts were designed and prepared aiming at using a second metal to prompt performance and suppress carbon formation. It was found Ni-Co combination has superior performance for CO_2-CH_4 reforming. Also, optimizing Ni-Co content can significantly reduce carbon formation leading to carbon free operation of CO_2-CH_4 reforming. The application of Ni-Co catalyst could significantly simplify process to achieve carbon free operation.

Materials and Methods

Catalysts were prepared by co-precipitating a common solution of metal cations. Elemental composition was determined by ICP-MS. Catalysts were tested in a quartz reactor with the inner diameter of 6 mm and products were analyzed using an on-line GC equipped with a TCD detector and a capillary column of 60 m in length. TEM and TG were employed for the analysis of carbon formation over spent catalysts.

Results and Discussion

The screening of catalysts was conducted over different combinations of metals such as Ni-Mn, Ni-Cu, Ni-Fe, and Ni-Co. It was found that Ni-Co combination has the best performances in terms of activity and selectivity. There is strong synergetic effect between Ni and Co, which can significantly improve the activity of catalysts for CO_2-CH_4 reforming [5]. Ni-Co catalysts have shown to be very stable for CO_2-CH_4 reforming in a 2000 h test at 750°C, 1 atm and GHSV=110,000 ml/g_{cat}-h with a feed gas of $CO_2/CH_4/N_2$=1/1/1 over catalyst-2. 2000 h time-on-stream experiment did not show any trend of deactivation.

Comparison of stability (Fig.1) indicated that catalyst-1 with lower Ni-Co content was more stable than catalysts with higher Ni-Co content at 750°C, 1atm, and GHSV=365,000 ml/g_{cat}-h.

BET analysis (Table1) indicated that catalyst-1 has higher specific surface area and smaller pore diameter, which are probably two of the factors affecting carbon formation rate (Table1 and Fig.2) and catalyst stability (Fig.1). The carbon formation rate of 0.000038g_{carbon}/g_{cat}-h over catalyst-1 was extremely low (Table1). TEM analysis (Fig.3) found carbon existing in the form of wisker-like carbon over catalyst-2 and -3, and carbon amount increasing with increase of Ni-Co content. However, there is no such kind of carbon observed over catalyst-1 by TEM analysis (Fig.3). The weight loss of catalyst-1 during TG analysis was probably caused by moisture. Therefore, carbon free operation of CO_2-CH_4 reforming can be achieved over Ni-Co catalysts by optimizing the Ni-Co content.

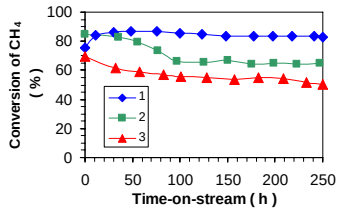

Fig.1 Comparison of stability

Table1. Surface area, pore diameter, and carbon formation rate

Catalyst	Elemental composition (mol%)				BET surface area (m^2/g)	Pore diameter (nm)	Carbon deposition rate (g_c/g_{cat}-h)
	Ni	Co	Al	Mg			
1	4	5	30	61	56	8.5	0.000038
2	6	9	28	57	54	9.0	0.001873
3	18	16	26	40	27	13.9	0.003844

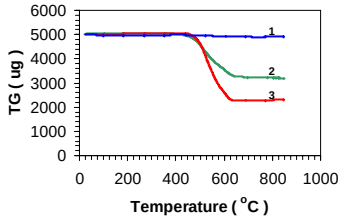

Fig.2 TG analysis for carbon

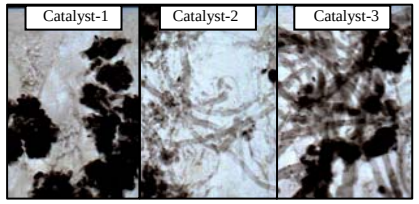

Fig.3 TEM analysis for carbon

Significance

The carbon free Ni-Co catalyst will prompt the industrial application of CO_2-CH_4 reforming technology both in new energy area and environmental protection area.

References

1. Vasileiadis, S., and Ziaka-Vasileiadou, Z. *Chem. Eng. Sci.* 59, 4853 (2004).
2. Ginsburg, J.M., Pina, J., Solh, T.E., and Lasa, H.I. *Ind. Eng. Chem. Res.* 44, 4846 (2005).
3. Teuner, S.C., Neumann, P, and Linde, F.V. *Oil Gas Eur. Mag.* 3, 44 (2001).
4. Udengaard, N.R., Hansen, J.-H. B., Hanson, D.C., and Stal, J.A. Oil and Gas Journal, 90, 62 (1992).
5. Becerra, A., Iriarte, M.E., Dimitrijewit, M., and Castro-Luna, A. *Bol. Soc. Chil. Quím.* 47, 385 (2002).