Production of Hydrogen Enrich Syngas by Methane Reforming over Multicomponent Co-Pt-based Supported Catalysts

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Abstract: The 5%Co-Pt/Al_2O_3-ZrO_2-CeO_2 catalysts with varying amount of Zr and Ce were prepared by impregnation method, characterized by a number of physico-chemical methods. The catalytic performance of Co-Pt/Al_2O_3-ZrO_2-CeO_2 catalysts was tested in the dry (DRM), steam (SRM), and bireforming of methane – combined dry and steam reforming (BRM). The synthesized catalysts perform the high activity, selectivity and stability in all the 3 processes studied with producing syngas with regulating H_2/CO ratio.
Keywords: Methane reforming, Hydrogen, Syngas.

1. Introduction

The major research efforts have been concentrated on the CO_2 and steam reforming of methane for hydrogen production [1]. The combination of these two reactions has substantial interest in alternative routes for the conversion of methane to hydrogen, which is a clean energy carrier [2].

The noble metals such as Rh, Pt, Ir, Pd, and Ru used as active components have been studied widely because of their resistance to coke formation. But their resource deficiency and high price restrain their industrial application. For this reason, the Co-based catalysts, which show good catalytic performances and are cheaper than noble metal catalysts, have been studied by many researchers. Noble metals in small amount may be used as a modifier. Also, CeO_2 and ZrO_2 have been reported as modifiers for the DRM catalysts, which can improve resistance of catalysts to the carbon deposition.

This work deals with the 5%Co-Pt/Al_2O_3-ZrO_2-CeO_2 catalysts studied in dry, steam and combined CO_2-steam (bireforming) reforming of methane to produce syngas with desired ratio of H_2/CO ratio.

2. Experimental

The multicomponent Co-containing catalysts were prepared by impregnating alumina modified by Ce and Zr additives with an aqueous solution of Co and Pt compounds. The total content of Co and Pt was equal to 5% and content of cerium and zirconium was varied within 2.5-7.5% from the total catalyst mass.

The processes were carried out in a flow reactor supplied with programmed heating and controlled feed velocity. The effect of temperature on the DRM, SRM and BRM with using a feed of $CH_4/CO_2/H_2O$=1/1/0÷1has been studied under atmospheric pressure, gas hourly space velocity (GHSV) was 1000 h^{-1}. Volume of the catalyst tested was 6 ml. Process duration was varied within 10-100 hours. The initial and final reaction products were online analysed using a GC's. The liquid products were analysed after their collection in a special cooling trap. The physico-chemical properties of the catalysts were studied by using a number of physico-chemical methods (X-Ray, H_2-TPR, SEM, TEM, BET).

3. Results and discussion

The 5%Co-Pt/Al_2O_3-ZrO_2-CeO_2 catalysts showed high activity in all three processes studied: DRM, BRM, and SRM. Temperature has the most effect on conversion of methane and carbon dioxide.

In the diagram (Figure 1), the comparison of the multicomponent 5%Co-Pt/Al_2O_3-ZrO_2-CeO_2 catalysts with varying amount of Ce and Zr is presented in DRM under the same conditions: t = 700°C, atmospheric pressure, space velocity of 1000 h^{-1} and a ratio of CH_4:CO_2=1.

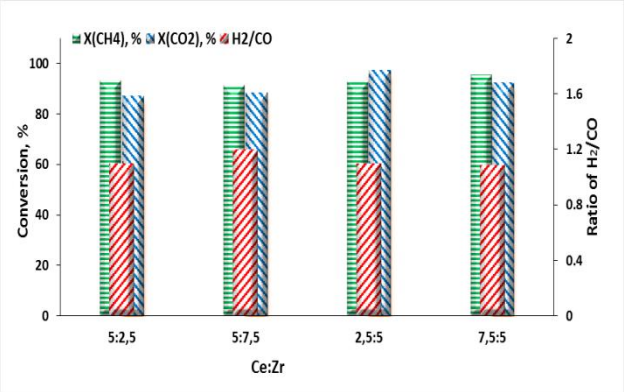

Figure1. Comparison of 5%Co-Pt/Al_2O_3-ZrO_2-CeO_2 catalysts in DRM (CH_4:CO_2=1:1, T=700°C, P = 0.1MPa, GHSV = 1000 h^{-1})

In DRM with use a feed of CH_4:CO_2=1, the CH_4 and CO_2 conversions are varied within 91.7-95.5 and 87.0-97.3% respectively, while in BRM with using a feed of CH_4:CO_2:H_2O=1:1:1 the CH_4 conversion is higher – 96.2-98.7% than CO_2 conversion, which varied within 87.0-91.3% depending the amount of Ce and Zr: t=700°C, P=0.1MPa, and GHSV=1000 h^{-1}. The catalysts produce the synthesis gas with the ratio H_2/CO>1 in both processes, in BRM syngas sufficiently is enriched with hydrogen.

The synthesized catalysts were also studied in SRM process and showed high activity and selectivity (Table 1).

Table 1. Comparison of the 5%Co-Pt(95:5)/Al_2O_3-Ce-Zr catalysts in SRM process (P=0.1 MPa, T=700°C, GHSV = 1000 h^{-1})

Catalyst	CH_4:H_2O	$X_{CH4,}$ %	H_2, %	H_2/CO
5%Co-Pt(95:5)/Al_2O_3-2.5%Ce-5%Zr	1:1	95.4	80	4.0
	1:1.5	83.1	76	3.1
5%Co-Pt(95:5)/Al_2O_3-7.5%Ce-5%Zr	1:1	98.5	83	4.8
	1:1.5	97.6	82	4.7
5%Co-Pt(95:5)/Al_2O_3-5%Ce-2.5%Zr	1:1	83.0	81	4.4
	1:1.5	88.6	79	3.7
5%Co-Pt(95:5)/Al_2O_3-5%Ce-7.5%Zr	1:1	89.8	78	3.6
	1:1.5	95.1	78	3.6

The 5%Co-M(95:5)/Al_2O_3-7.5%Ce-5%Zr catalyst has been continuously tested in DRM and BRM for a period of more than 100 hours to determine the stability of the catalyst. No loss of activity and selectivity of have been observed.

4. Conclusions

The 5%Co-Pt/Al_2O_3-ZrO_2-CeO_2 catalysts perform the high activity and stability in all processes studied: dry, steam, and bireforming of methane. That allows producing syngas with a required H_2/CO ratio depending on a feed composition and subsequent needs. Thus, by varying the ratio of CO_2:H_2O within 0÷1/0÷1.5 the resulting H_2:CO ratio is tuned from 1.0 to 4.8, covering a wide range of syngas ratios relevant to various applications.

References

1. C. Gennequin, M. Safariamin, S. Siffert, A. Aboukaïs, E. Abi-Aad, Catal. Today 176 (2011) 139.
2. C.S. Lau, A. Tsolakis, M.L. Wyszynski, Inter. J. of Hydrogen Energy 36 (2011) 397.