Effects of Preparation Conditions and Ni/Co Ratio on Ni-Co Bimetallic Catalyst Performance for CO_2 Reforming of CH_4

Chunyu Xi and Hui Wang*
University of Saskatchewan, Saskatoon, Saskatchewan, S7N 5A9 (Canada)
* hui.wang@usask.ca

Introduction

Carbon dioxide (CO_2) reforming of methane (CH_4) has recently received considerable attention since it consumes CO_2 and CH_4, the major component of greenhouse gases [1]. Most reported researches have been concentrated on non-noble metal catalyst, especially nickel due to the comparable activity and stability but the lower price [2]. However, nickel-based catalysts easily induce carbon formation, causing catalyst deactivation. Therefore, many attempts have been made to suppress carbon formation over Ni-based catalysts. Our group has reported a very stable and highly active Ni-Co bimetallic catalyst of a general formula Ni-Co-Al-Mg-O prepared by coprecipitation method that has undergone 2000 h stability test for CO_2 reforming of CH_4 where no significant deactivation was observed [3, 4].

Focusing on the Ni-Co/AlMgOx bimetallic catalysts developed in our previous work, this work further investigates the effects of catalyst preparation conditions such as pH of precipitating solution, the Ni/Co ratio and the catalyst reduction temperature on catalyst performance. The optimal condition to prepare Ni-Co/AlMgOx bimetallic catalysts is achieved.

Materials and Methods

Ni-Co/AlMgO$_x$ bimetallic catalysts with different Ni/Co ratios were prepared by using conventional coprecipitation method with aqueous ammonia solution as precipitating agent. The pH value of the precipitating solution was controlled in the desired rang, And the precipitation was carried out at room temperature (22-24 °C). The precipitates was dried and calcined in air at 900 ºC for 6 h. The evaluation of catalyst activity and stability was carried out in a bench-top fixed-bed quartz microreactor (Autoclave) with an i.d. of 6 mm. The product gas was analyzed by an on-line Agilent 6890N GC equipped with TCD and ShinCarbon ST 100/120 mesh 2 m × 1 mm ID micropacked GC column.

Results and Discussion

It has been known that the pH value of the solution significantly affect states of metal hydroxide using coprecipitation method. In this work, it is found that sol-gel was formed when the pH of solution was controlled less than 8.0 or more than 9.0. Precipitation only occurred and loose power was formed after drying when the pH range of the solution was 8.0-9.0. Thus, 8.0-9.0 pH range was chosen for precipitation. The effect of Ni/Co ratios on performances of the catalysts (Table 1) clearly indicates that the catalyst with Ni/Co=1 has highest activity. We think that the Co addition is beneficial to dilution of the ensembles of Ni atoms and to the stability of Ni. But more Co added (Ni/Co<1) will lead to decreasing of active sites on catalyst surface, which would affect the catalyst performance. Fig. 1 suggests that catalyst reduction temperature has effects on the catalytic performance: the catalyst reduced at 800 °C shows the best performance. Because catalyst reduction temperature is closely related to the metal dispersion, the metal particle size and the interaction between the two metal atoms, which may affect the activity and stability of the catalysts.

Table 1. The elemental composition and CH_4 conversion[a] (50 h on stream) of Ni-Co bimetallic catalyst with various Ni/Co ratios

Catalyst	Ni (mol %)	Co (mol %)	Mg (mol %)	Al (mol %)	Ni/Co	CH_4 Conversion [a]
A	2.35	4.97	65.40	48.50	0.47	25.1 %
B	3.39	3.75	62.08	49.20	0.90	69.1 %
C	4.78	2.24	63.31	44.44	2.13	53.3 %

a: The reaction conditions: T = 750 ºC, P = 1 atm, GHSV=558,000 ml/g.h, Time = 50 h, $H_4/CO_2/N_2$ = 1:1:1, 0.02 g catalyst.

Significance

This work will lead to the preparation of industrial catalysts for CO_2 reforming of CH_4, where optimal preparation parameters are necessary.

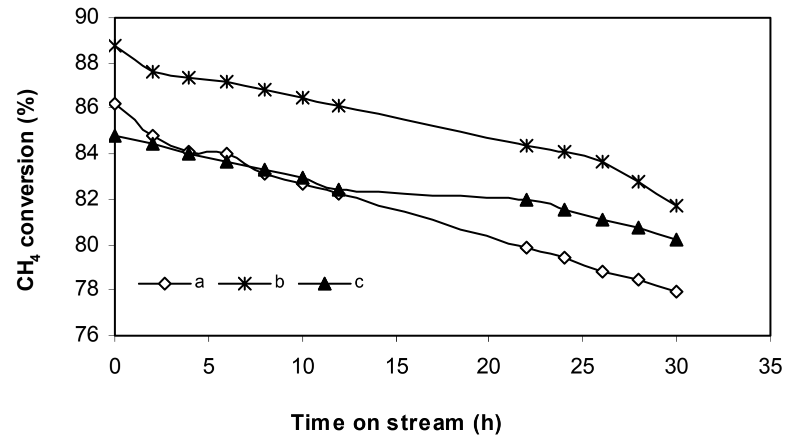

Figure 1. Stability of the catalyst with Ni/Co=0.90 under different reduction temperatures: (a) 750 °C; (b) 800 °C; (c) 850 °C. The reaction conditions: P=1 atm, GHSV=558,000 ml/g.h, $H_4/CO_2/N_2$= 1:1:1, 0.02g catalyst.

References

1. Ashcroft, A.T., Cheetham, A.K., and Green, M.L.H. *Nature* 352, 225 (1991).
2. Bradford, M.C.J., and Vannice, M.C.J. *Catal. Rev.Sci.Eng.* 41, 1 (1999).
3. Zhang, J.G., Wang, H., and Dalai, A.K. *J. Catal.* 249, 300 (2007).
4. Zhang, J.G., Wang, H., and Dalai, A.K. *Appl. Catal. A: General* 339, 121 (2008).