



## Carbon Dioxide Reforming of Methane Over Bimetallic Co-X/Activated Carbon Catalysts (X = Ni, Cu, Fe, Mg, Ca)

GUOJIE ZHANG\*, YANNIAN DU and YONGFA ZHANG

Key Laboratory of Coal Science and Technology, Ministry of Education and Shanxi Province, Taiyuan University of Technology, Taiyuan, P.R. China

\*Corresponding author: Tel/Fax: +86 351 6018676; E-mail: zhangguojie@tyut.edu.cn; zhgjdoc@126.com

Received: 1 May 2013;

Accepted: 22 July 2013;

Published online: 15 April 2014;

AJC-15005

Carbon dioxide reforming of methane has been studied over Co/activated carbon catalysts promoted with different metal additives (Ni, Cu, Mg, Ca, Fe) aiming to improve the performance of the catalysts and increase their resistance to coking. It was found that the type of the promoter significantly affected the metal dispersion properties and catalytic performances of Co/activated carbon catalysts in the temperature range of 750-850 °C. Nickel doped Co/activated carbon displayed the highest activity among all the catalyst. This is mainly result due to nickel-cobalt formation alloy.

**Keywords:** Activated carbon, Reforming, Methane, Activity, Bimetallic.

### INTRODUCTION

Since 1993 China has been the largest coke producer in the world. While a large number of independent coking plants were built, a large number of coke oven gas could not be utilized effectively<sup>1</sup>. The emission of coke oven gas not only pollutes the environment, but also wastes precious fossil fuel resources. However, one of the ways of chemical utilization of coke over gas is transformation into synthesis gas (H<sub>2</sub> + CO). Compared with partial oxidation and steam reforming of CH<sub>4</sub>, the synthesis gas produced from CO<sub>2</sub> reforming methane (dry reforming, DR) has a great advantage. Its production gas of H<sub>2</sub>/CO ratio is close to 1, which is more suitable for F-T synthesis for production of liquid hydrocarbons<sup>2-4</sup>. So dry reforming has been a focus issue in recent years.

The major limitation of dry reforming is the requirement of high temperature to reach high conversion levels because of that the highly endothermic nature of the process. The harsh operating conditions results in two adverse outcomes: one is coke deposition from cracking of CH<sub>4</sub> and the other is sintering of the metallic phase and support. Both of the outcomes devote to the deactivation of catalyst in a short period of time. Even though the noble metal-based catalysts (such as Rh and Pt) can provide high activity and selectivity with almost no carbon deposition, they are not favorable for large scale commercial use<sup>5-8</sup>, the main reasons are the limited availability and high cost of their active noble metals. Thus, developing non-noble metal-based catalyst is more imperative.

Activated carbon has many advantages, such as developed pore structure, giant specific surface area, sufficient heat resistance at the high temperature of 500-600 °C, acid and alkali corrosion, which are unmatched by other carriers<sup>9</sup>. In addition, activated carbon has a high melting point, which can minimize the sintering of metal or metal oxide aggregates on the surface. This work is to design and develop a bimetallic Co-based dry reforming catalyst supported on activated carbon, to improve the performance of the Co-based catalysts and reduce energy consumption in large-scale commercial use.

### EXPERIMENTAL

**Catalyst preparation** A series of Co-X/active carbon catalysts were prepared by the wetness co-impregnation method (X = Ni, Cu, Fe, Mg, Ca). The active carbon carriers (15-35 mesh) were impregnated with a solution containing cobalt nitrate and precursor of the metal additives (nickel nitrate, copper nitrate, iron nitrate, calcium nitrate and magnesium nitrate) for 12 h. After the impregnation step, the samples were dried overnight at 110 °C. Activated carbon characteristics are presented in Table-1 and experimental device is shown in Fig. 1.

**Catalytic activity test:** The catalysts in the fixed bed reactor was heated under normal pressure at the rate of 10 °C/min to 650 °C with a flow of H<sub>2</sub>, and stayed for 60 min at 650 °C, finally, a gas mixture of CH<sub>4</sub>:CO<sub>2</sub> (1:1) was passed over the catalyst bed at a total flow rate of 120 mL/min. The reaction

Proximate analysis (wt. %)			Ultimate analysis (wt. %)				
M <sub>ad</sub>	A <sub>d</sub>	V <sub>ad</sub>	F <sub>cd</sub>	H <sub>d</sub>	N <sub>d</sub>	S <sub>d</sub>	O <sub>d</sub>
1.30	7.67	1.72	80.59	0.91	0.35	0.50	0.35

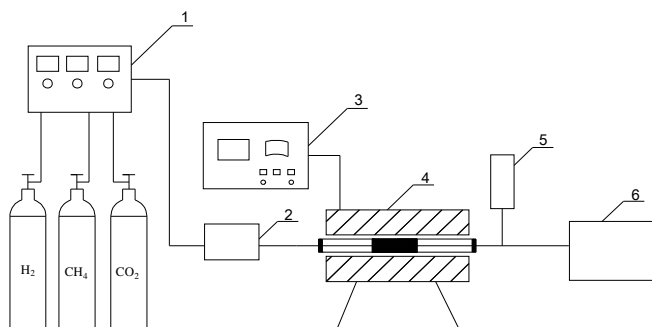


Fig. 1. Experimental device flowchart. 1. Mass flow controller. 2. Gas mixer. 3. Temperature controller. 4. Fixed bed reactor. 5. Soap suds flow meter. 6. Gas chromatography

gas products were analyzed every 50 °C with an online chromatograph equipped with a TCD and a 5A-molecular sieve packed column. The conversion rate of feed gas is calculated by

$$X = \left( 1 - \frac{F_{\text{out}} C_{\text{out}}}{F_{\text{in}} C_{\text{in}}} \right) \times 100 \%$$

where: X-feed gas conversion, %; F<sub>out</sub>-product gas flow, mL/min; F<sub>in</sub>-feed gas flow, mL/min; C<sub>out</sub>-content of the feed gas, mol/L; C<sub>in</sub>-content of product gas, mol/L.

## RESULTS AND DISCUSSION

Figs. 2 and 3 show the CH<sub>4</sub> and CO<sub>2</sub> conversion and the H<sub>2</sub>/CO ratio in the product gas as a function of reaction temperature, respectively. The different activity levels of the catalysts show that the catalytic performance of promoted-Co/active carbon strongly depends on the type of the metal additive used. The order of methane conversion is Ni > Cu > Fe > Ca > Mg in the temperature range of 750-850 °C over cobalt-based catalysts in terms of the type of promoters added. There may be two reasons for this phenomenon, firstly, Ni is known to be a material with high activity in reforming reaction; secondly, Ni and Co have the similar ionic radius, which are easy to form the Ni-Co alloy. The forming alloy inhibits the migration of the active ingredient in the carrier surface under high temperature conditions and increases the dispersion degree of the active ingredient in the carrier surface. The Ni-Co alloying during reduction renders the separate metal ensembles in metal particles even smaller and the small metal particles enhances the CO<sub>2</sub> activation, all of which leads to complete inhibition of carbon deposition without sacrificing the activity. Chen *et al.*<sup>10</sup> draw the similar conclusion from the parallel investigation, the formation of homogeneous metal alloy on the bimetallic catalysts was observed after the reduction and catalysts with higher Co/Ni ratios showed smaller active metal particle sizes. In addition that, it is noteworthy that the Co-Ni/active carbon catalyst led to the highest H<sub>2</sub>/CO ratio at 650 °C, then the H<sub>2</sub>/CO ratio approaching 1 with increasing reaction temperature. This is mainly due to the influence of reaction tempe-

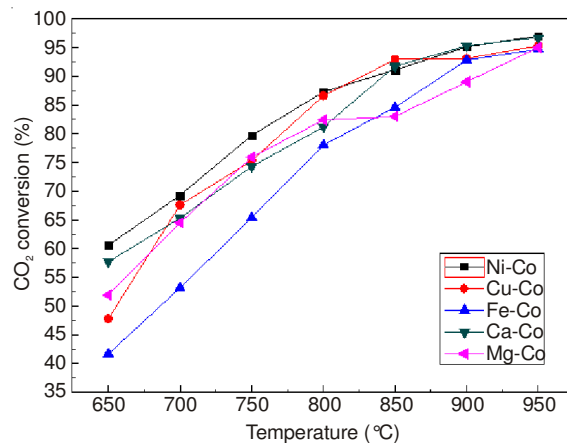
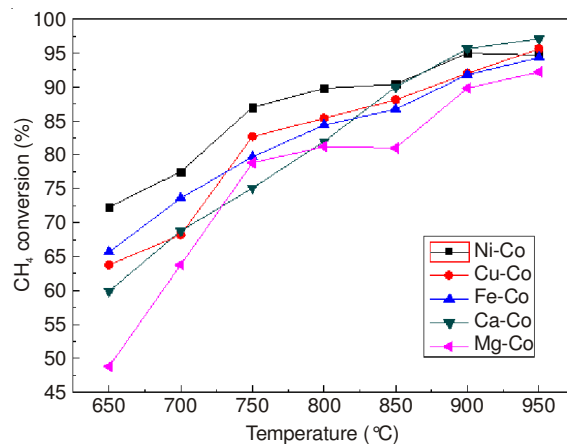


Fig. 2. Effect of different active composite metal on the conversion of CH<sub>4</sub> and CO<sub>2</sub>

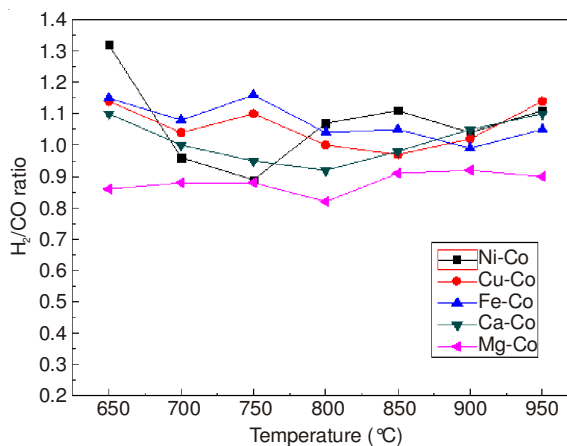


Fig. 3. Effect of different active composite metal on the H<sub>2</sub>/CO ratio

rate. Fig. 2 shows that the conversion of CH<sub>4</sub> and CO<sub>2</sub> is 73 and 60 %, respectively at 650 °C. It is widely accepted that the initial reforming temperature under normal pressure is 640 °C, so the Ni-Co alloy or single metal devotes to a lot in reducing activation energy, which is the reason of that conversion of CH<sub>4</sub> and CO<sub>2</sub> reaches so high at initial temperature. Before 650 °C, first occurrence of methane decomposition reaction to form carbonaceous species and H<sub>2</sub>, then carbonaceous species react with carbon dioxide to produce CO. When the reaction temperature is higher than 650 °C, CO<sub>2</sub> reforming of CH<sub>4</sub> began reforming reaction and which took the dominant role in reforming reaction system. The result was that H<sub>2</sub>/CO ratio was gradually approaching 1.

## Conclusion

The carbon dioxide reforming of methane over bimetallic Co-X/activated carbon catalysts (X = Ni, Cu, Fe, Mg, Ca) may be summarized as follows: The type of the metal additive used significantly affected the metal dispersion properties and catalytic performances of promoted-Co/activated carbon catalysts. Monometallic Co/activated carbon had high initial activity but it suffered from severe carbon deposition. Ni-modified catalyst exhibited high activity among all the catalysts in the temperature range of 750-850 °C. As it mainly result due to nickel-cobalt formation alloy on the support.

## ACKNOWLEDGEMENTS

This work was supported by the Natural Science Foundation of China (21006066) and Shanxi Provincial Natural Science Foundation (2011021009-2).

## REFERENCES

1. J. Shen and Z.Z. Wang, *Energy Fuels*, **21**, 3588 (2007).
2. S. Özkara-Aydinoglu, E. Özensoy and A.E. Aksoylu, *Int. J. Hydrogen Energy*, **34**, 9711 (2009).
3. M.C.J. Bradford and M.A. Vannice, *J. Catal.*, **173**, 157 (1998).
4. S.M. Stagg-Williams, F.B. Noronha, G. Fendley and D.E. Resasco, *J. Catal.*, **194**, 240 (2000).
5. A.T. Ashcroft, A.K. Cheetham, M.L.H. Green and P.D.F. Vernon, *Nature*, **352**, 225 (1991).
6. M. García-Diéguez, I.S. Pieta, M.C. Herrera, M.A. Larrubia and L.J. Alemany, *J. Catal.*, **270**, 136 (2010).
7. Z. Hou, P. Chen, H. Fang, X. Zheng and T. Yashima, *Int. J. Hydrogen Energy*, **31**, 555 (2006).
8. G. Zhang, Y. Dong, M. Feng, Y. Zhang, W. Zhao and H. Cao, *Eng. Chem. J.*, **156**, 519 (2010).
9. B. Fidalgo and J.Á. Menendez, *Chin. J. Catal.*, **32**, 207 (2011).
10. L. Chen, Q. Zhu and R. Wu, *Int. J. Hydrogen Energy*, **36**, 2128 (2011).