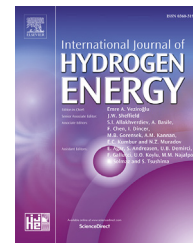




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Effect of different activated carbon support on CH₄–CO₂ reforming over Co-based catalysts



Yinghui Sun ^a, Guojie Zhang ^{a,b,*}, Jiwei Liu ^a, Peiyu Zhao ^a, Peng Hou ^a, Ying Xu ^a, Riguang Zhang ^a

^a Key Laboratory of Coal Science and Technology, Ministry of Education and Shanxi Province, Taiyuan University of Technology, Taiyuan 030024, China

^b State Key Laboratory of Coal and CBM Co-Mining, Jincheng 048012, China

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ABSTRACT

CH₄–CO₂ reforming to syngas was investigated over three different activated carbon catalysts. To better understand the influence of the supports on the catalytic properties, catalysts were analyzed by some characterization methods, such as nitrogen adsorption–desorption isotherms, XRD, H₂-TPR, NH₃-TPD, CO₂-TPD, FTIR, TEM and EDX. The results showed that the catalyst with AC₂ as the support provided the best catalytic activity. The CH₄ conversion and CO₂ conversion were 92% and 98% at 900 °C, respectively; best selectivity with the H₂/CO ratio was close to 1 among the three supports used. It also showed a better stability at 900 °C. H₂-TPR analysis showed that Co species in Co/AC₂ catalyst were strong interaction with the support. It was observed that active metals were well dispersed on the AC₂ support by the TEM. In addition, the ratio of CH₄/CO₂ also had great influence on the CH₄ and CO₂ conversion.

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Introduction

CO₂–CH₄ reforming (DRM) obtained considerable attention due to the environmental, economic and energetic benefits. First of all, CO₂–CH₄ reforming is important because CH₄ and CO₂ could be converted to syngas process [1,44]. Compared with other reforming technology, the hydrogen/carbon ratio of CO₂–CH₄ reforming is always close to 1. The syngas could also be used for the synthesis of fuel through F-T process [2,3]. Moreover, DRM reaction provides the possibility of utilization natural gas with high CO₂ content, avoiding the complex and expensive gas fractionation operation. DRM reaction is also an

attractive method of using coke oven gas [4], a clear and environmentally-friendly energy that is manufactured usually from coal coking and mainly composed of CO₂ and CH₄ [5]. However, the large scale industrial application of DRM technology is limited by the deposition of carbon and active metal sintering. The major obstacle preventing large-scale industrial application of the DRM is the inability to develop a catalyst with high catalytic activity. Several factors, such as the species of active metal, carrier and active ingredient particle size affected the catalytic performance and carbon deposition [6].

Traditional non-precious metals such as Ni, Co, and Fe [7–10] also show excellent catalytic activity, though the stability is lower than noble metal (Ru, Au, Rh, Pt and Pd) [11–15].

* Corresponding author. Key Laboratory of Coal Science and Technology, Ministry of Education and Shanxi Province, Taiyuan University of Technology, Taiyuan 030024, China.

E-mail addresses: zhangguojie@tyut.edu.cn, zhgidoc@126.com (G. Zhang).

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Non-precious metals become an appropriate alternative for the large-scale commercial application due to their competitive prices. Supported catalysts based on Ni as active phase, and Al_2O_3 , CeO_2 , ZrO_2 , SiO_2 [16–19] and zeolite as support have shown high activities for reforming reaction but frequently accompanied by quickly deactivation. Previous investigations have shown that Co catalyst also have good catalytic property and the formation mechanism of carbon deposition on Co active species is different from Ni catalyst [20–24], so Co-based catalyst is one of the most potential material for DRM reaction.

To obtain higher metal dispersion, various supports such as Al_2O_3 and SiO_2 for Co-based catalysts have been utilized in DRM reaction. A number of researchers have concentrated on Cobalt-based catalysts supported on SiO_2 or Al_2O_3 support [20,25–28]. For this kind of supports, the major problem is that it is easy to form hardly reducible materials such as CoAl_2O_4 or Co_2SiO_4 , due to the strong mutual effect among components of Co-based catalysts, the catalytic efficiency and activity were restricted. Research result by San José-Alonso et al. [29] demonstrated that catalyst with 1% Co content deactivated during the first minutes of the DRM reaction at 700 °C, because Co united with Al_2O_3 to form CoAl_2O_4 , which the active sites were decreased. Wang et al. [30] reported that Co_3O_4 was generated as a major phase when the calcination temperature was 500 °C and $\gamma\text{-Al}_2\text{O}_3$ supported Co as catalyst. The Co_2AlO_4 and CoAl_2O_4 were generated when the roasting temperature was 1000 °C. The reduction ability of the Co/ $\gamma\text{-Al}_2\text{O}_3$ lowered with the calcination temperature rising, because of the production of irreducible Co_2AlO_4 and CoAl_2O_4 . Bouarab et al. [31] reported that cobalt phase was sintered and the particular medium basicity of the silicate interphase allows an irreversible storage of a pool of hydrogen-carbonates in the locality of cobalt particles, when Co/ SiO_2 used as catalyst.

Carbon materials such as activated carbon (AC) [32,33], carbon nanotubes (CNT) [34,35], carbon nanospheres (CNS) [36], carbon nanofibers (CNF) [37,38], graphene oxide (GO) [39] etc. have large surface area, high stability and excellent chemical inert. Moreover, the chemical properties of carbon materials can be easily modified. Recently, it has been demonstrated that activated carbon is effective for oxygen reduction [40–42]. To further enhance the catalytic activity of AC, one of the most promising strategies is to combine with active metal for oxidation-reduction reaction. Song et al. [43] has reported that the AC bring forward a better catalytic performance than the coal char, the reforming temperature of reaction has a significant impact on the methane and carbon dioxide conversions. The carbon deposition was alleviated, when the reaction temperature was over 950 °C.

The performance of cobalt-based catalysts is seriously influenced by the carrier's structure, especially mesoporous and microporous structures. However, the influence of using carbonaceous materials with good thermal and chemical stability as carrier and supported cobalt species for DRM reaction catalysts, the structure and catalytic characteristic were still not clear. Especially the reports of the catalytic performance on different carbonaceous carrier supported Co species for the DRM reaction was not found in the

available literature. Here three different types of activated carbon with varied textural properties were selected, as the cobalt-based catalysts supports to study the influence of supports on DRM catalytic activity and stability.

Experimental

Preparation of Co-based/AC catalysts

Three different types of activated carbon were obtained from market. Two of them (AC_1 and AC_2) were prepared from different types of coal (AC_1 from Jiaozuo Activated Carbon Company, Henan; AC_2 from Xinhua Activated Carbon Company, Shangxi), another one (AC_3) was prepared from coconut husk (AC_3 from Hunan Activated Carbon Company, Hunan). Analytical pure $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was obtained from Aladdin Industrial Corporation (Shanghai, China). Distilled water was prepared from Ulupure water purified machine (Chengdu, China). Three different types of activated carbon were washed with distilled water several times, then were dried at 105 °C in a vacuum drying oven. Co supported catalysts were successfully prepared by an excessive impregnation method. 20 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 70 mL of distilled water, and 20 g activated carbon was added to the solution with constantly stirring at room temperature for 5 h. Then the catalysts were dried at 110 °C for 12 h and calcined at 500 °C for 200 min in nitrogen atmosphere. The catalysts are named as Co/AC_x, x refers to the type of AC.

Catalytic activity test

To determine the catalytic activity and stability of the Co/AC_x for DRM reaction, 10 g catalysts was packed into a quartz (Diameter about 25 mm). Before activity study, the samples were reduced in situ at 650 °C under H_2 flow for 1 h under pure hydrogen (60 mL/min). Then, 120 mL/min flow of both CH_4 and CO_2 (molar ratio = 1:1) without dilution was introduced. The reforming reaction was studied by increasing the temperature from 650 °C to 900 °C with 10 °C/min heating rate. Prior to test, the temperature was maintained for 50 min. The concentrations of the feed and product streams were measured through a gas chromatograph (GC-950, Shanghai Haixin Instrument) with TCD and FID detector using carbon molecular sieves column. The temperature of the column was set at 60 °C with argon used as carrier gas. In this study, the carbon dioxide and methane conversions were counted based on the following formulas:

$$X_{\text{CH}_4} = \left(1 - \frac{F_{\text{out}} \cdot C_{\text{CH}_4, \text{out}}}{F_{\text{in}} \cdot C_{\text{CH}_4, \text{in}}} \right) \times 100\% \quad (1)$$

$$X_{\text{CO}_2} = \left(1 - \frac{F_{\text{out}} \cdot C_{\text{CO}_2, \text{out}}}{F_{\text{in}} \cdot C_{\text{CO}_2, \text{in}}} \right) \times 100\% \quad (2)$$

where X_{CH_4} and X_{CO_2} are the conversion of CH_4 and CO_2 , respectively; F_{out} and F_{in} are the final and initial flow, respectively; $C_{\text{CO}_2, \text{out}}$ and $C_{\text{CO}_2, \text{in}}$ refer to the final and initial concentration of CO_2 respectively; $C_{\text{CH}_4, \text{out}}$ and $C_{\text{CH}_4, \text{in}}$ refer to the final and initial concentration of CH_4 .

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