

Influence of Ni based catalysts on CH₄-CO₂ reforming reaction

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ABSTRACT: The nickel based catalysts were prepared by the method of impregnation. The influence of the Ni loading, the calcination temperature, the reduction temperature, the promoter on the catalyst performances in the CH₄-CO₂ reforming reaction was investigated. The results indicate that the Ni/SiO₂ catalyst with the 10%Ni loading and calcined at 773 K for 2 h and reduced at 723 K for 2 h exhibited the best activity in the reaction, and the conversion of CH₄, CO₂ and total carbon were 67.27%, 67.21%, 67.24%, respectively. The influence of the Cr₂O₃ promoter on the properties of the catalysts was investigated. The results show that the carbon deposition on the Ni/SiO₂/Cr₂O₃ catalyst was decreased, and the activity of the catalyst was enhanced by adding Cr₂O₃ promoter in the Ni/SiO₂ catalyst. The conversion of CH₄, CO₂ and total carbon reached 69.86%, 70.47% and 70.20% on the Ni/SiO₂/Cr₂O₃ catalyst with the 10% Ni and 1.0% Cr₂O₃ calcined at 773K for 2 h and reduced at 723K for 2 h in the CH₄-CO₂ reforming reaction. The carbon deposition on Ni/SiO₂/Cr₂O₃ catalyst was decreased 26.35% compared to that on Ni/SiO₂ catalyst.

INTRODUCTION

Because of the continuous and rapid CO₂ emission with the growing of world population and the development of civilization and industrialization, the greenhouse effect is enhanced. therefore, strong interest has been shown in controlling and utilizing the greenhouse gases (Arkatova 2010, Fidalgo and Menendez 2011, Havran, Dudukovic and Lo 2011, Huang et al. 2011, Pinheiro et al. 2009). The CO₂-CH₄ forming reactions can consume two kinds of greenhouse gases. Furthermore, the product syngas can be used as a feed-stock for some industrial processes of chemistry such as the Fischer-Tropsch synthesis, and Methanol synthesis (Sarkar et al. 2012, Wang et al. 2012). Nevertheless, the CH₄-CO₂ forming reactions have not been industrialized due to the rapid carbon deposition deactivation on the catalysts (Jabbour et al. 2015, Estephane et al. 2015). According to previous studies, comparing to non-noble catalyst, some noble catalysts i.e. Ru, Pd, Pt and Rh exhibit better performance in terms of the conversion and selectivity of CH₄ and carbon deposition resistance. However, the high cost and difficult recycling for the noble catalysts restricts their industrial application (Mette et al. 2015). Therefore, Effective and stable non-noble metal catalysts are more and more attention.

It is investigated that nickel based catalyst deactivation due to carbon deposition and active metal sintering (Yu et al. 2015, Wang et al. 2015). However, Ni based catalysts are abundant and low cost, and exhibit high activity in the CH₄-CO₂ reforming reactions. therefore, the development of carbon deposition resistant and sintering resistant Ni based catalysts for the CO₂ reforming reaction of CH₄ is of great importance.

For the past years, many studies about the CH₄-CO₂ reforming reactions on Ni based catalysts have shown that loadings, supports, promoters, the calcination temperature and reduction temperature may lead a key effect on the activity and the carbon deposition resistance. The loadings of Ni can't be too low, which may lead to low activity of the catalyst. Certainly, it can't be too high, which makes Ni atoms low dispersion that leading to sintering easily. The catalysts of acidic surface produce more carbon deposition after the reaction. Meanwhile, acidic supports contribute to improving the activity of catalyst. Promoters can improve Ni-based catalyst carbon deposition resistance by reducing the surface acidity of catalyst or improving the dispersion of Ni atoms and the increasing of

metal surface area (Paksoy, Caglayan and Aksoylu 2015). The calcination temperature and reduction temperature influence the activity of the catalyst. If the temperature is low, the Ni-salt/NiO can't be decomposed/reduced completely, but if the temperature is too high, the Ni atoms may be sintering into Ni-spinel. For example, catalyst NiO/ γ -Al₂O₃ calcined at 1023 K, it will turn into spinel NiAl₂O₄ with extreme activity of methane reforming.

In this study, a series of Ni/SiO₂ catalysts with different Ni loadings and Ni/SiO₂/Cr₂O₃ catalysts with different Cr₂O₃ loadings were prepared by the method of impregnation at different calcination temperature and reduction temperature in order to investigate their performances in the CH₄-CO₂ reforming reactions.

EXPERIMENTAL

Catalyst preparation

The Ni/SiO₂ catalysts were prepared by the method of impregnation of SiO₂ (20~40 mesh, surface area 379.244 m²/g, pore volume 1.039 ml/g, pore diameter 12.483 nm) with the aqueous solution of nickel nitrate, which Ni loadings were 3%, 7%, 10%, 13%, 17%, respectively. Subsequently, the impregnated solids were dried at 393K at room temperature for 12 h, calcined in air at a certain temperature for 2 h and reduced in the atmosphere of 99.999% H₂ at a certain temperature for 2 h.

Ni/SiO₂/Cr₂O₃ catalysts were prepared by the method of impregnation of SiO₂ with the mixture aqueous solution of nickel nitrate and chromium nitrate, which Cr₂O₃ loading was 0.5% (wt), 1.0%, 1.5%, 2.0%, 2.5%, respectively. Subsequently, the impregnated solids were dried at 393 K at room temperature for 12 h, calcined in air at optimum temperature for 2 h and reduced in the atmosphere of 99.999% H₂ at optimum temperature for 2 h.

Catalytic activity measurements

The CH₄-CO₂ reforming reaction was implemented under atmospheric pressure in a quartz-tube (internal diameter: 12 mm) fixed-bed reactor at 973 K for 4 h. The Ni/SiO₂ catalyst (0.2 g) was reduced in situ by H₂ at the reduction temperature for 2 h before the reaction. The reactor was heated to the set temperature after the reduction. A reactant gas CH₄/CO₂/Ar (44.0/47.2/8.8) flowed into the fixed-bed reactor at a flow velocity of 50 ml min⁻¹, in which argon was regard as an internal standard for the further calculation.

The product gas component from the fixed-bed reactor through the air set pipe and ice-water-cooled trap successively was analyzed on a gas chromatograph (GC-TCD) on line. The conversion of CH₄, CO₂ and total carbon was calculated as follows:

$$CH_4 \text{ conv.} = \frac{CH_4/Ar \text{ in feed} - CH_4/Ar \text{ in effluent}}{CH_4/Ar \text{ in feed}} \times 100\% \quad (1)$$

$$CO_2 \text{ conv.} = \frac{CO_2/Ar \text{ in feed} - CO_2/Ar \text{ in effluent}}{CO_2/Ar \text{ in feed}} \times 100\% \quad (2)$$

$$C_{\text{total}} \text{ conv.} = CH_4 \text{ conv.} \times \frac{a}{a+b} + CO_2 \text{ conv.} \times \frac{b}{a+b} \quad (3)$$

(a and b were the contents of CH₄ and CO₂ in the feed gases, respectively).

RESULTS AND DISCUSSIONS

Influence of Ni content in Ni/SiO₂ catalysts on the reaction

Table 1 shows the results of the CH₄-CO₂ reforming reactions which was implemented at 973 K and ordinary pressure (0.1 MPa) for 4 h using the Ni/SiO₂ catalysts with different Ni loadings, which were calcined in air at 673 K for 2 h and reduced in the atmosphere of 99.999% H₂ at 773 K for 2 h at a heating rate of 10 K/min both.

Table 1 shows that the conversion of CH₄, CO₂ and total carbon increased when Ni loadings increase from 3% to 10%. However, the conversion of CH₄, CO₂ and total carbon decreased when Ni loading

increase from 10% to 15%. But the carbon deposition increased with Ni loading increasing from 3% to 15% roughly. That is, the Ni/SiO₂ catalyst was favorable for the CO₂ reforming reaction of CH₄ when the Ni loading is 10%, and the conversion of CH₄, CO₂ and total carbon of 62.76%, 66.93%, 65.20%, respectively, and the carbon deposition of 0.3121 g were obtained on the 10%Ni/SiO₂.

Table 1. Influence of Ni loading in Ni/SiO₂ catalysts in the reaction.

| Ni loading /% | CH ₄ conv./% | CO ₂ conv./% | C _{total} conv./% | carbon deposition/g |
|---------------|-------------------------|-------------------------|----------------------------|---------------------|
| 3% | 50.71 | 62.45 | 57.48 | 0.3058 |
| 7% | 61.12 | 64.26 | 62.93 | 0.3144 |
| 10% | 62.76 | 66.93 | 65.20 | 0.3121 |
| 13% | 57.10 | 66.00 | 62.21 | 0.3302 |
| 15% | 57.12 | 65.34 | 62.28 | 0.3320 |

Reaction conditions: Mass of catalyst, 0.2 g; Reaction temp., 973 K; Reaction pressure, 0.1 MPa; Reaction time, 4 h; Reactant gas, CH₄/CO₂/Ar = 44.0/47.2/8.8, 40 ml min⁻¹. The conversions listed here were the average values during a 4h reaction.

Influence of calcination temperature in 10%Ni/SiO₂ catalysts in the reaction

Table 2 shows the results of the CO₂ reforming reaction of CH₄ which was implemented at 973 K and ordinary pressure (0.1 MPa) for 4 h with 10%Ni/SiO₂ catalysts at different calcination temperature, 673 K, 723 K, 773 K, 823 K, 873 K, respectively, and reduced in the atmosphere of 99.999% H₂ at 773 K for 2 h at a heating rate of 10 K/min both.

Table 2 shows that the conversion of CH₄, CO₂ and total carbon increased with the calcination temperature rising from 673 K to 773 K roughly, and then decreased when the calcination temperature rised from 773 K to 873 K with almost opposite tendency of the carbon deposition. Therefore, when the 10%Ni/SiO₂ catalyst was calcined at 773K, it was favorable for the CH₄-CO₂ reforming reaction, and the conversion of CH₄, CO₂ and total carbon achieved 67.16%, 64.40%, 65.59%, respectively, and the carbon deposition was 0.2750 g.

Table 2 Influence of calcination temperature in 10%Ni/SiO₂ catalysts in the reaction.

| C.T. /K | CH ₄ conv./% | CO ₂ conv./% | C _{total} conv./% | carbon deposition/g |
|---------|-------------------------|-------------------------|----------------------------|---------------------|
| 673 | 62.76 | 66.93 | 65.20 | 0.3121 |
| 723 | 64.92 | 63.99 | 64.39 | 0.3115 |
| 773 | 67.16 | 64.40 | 65.59 | 0.2750 |
| 823 | 66.14 | 66.14 | 66.14 | 0.3160 |
| 873 | 63.84 | 65.34 | 64.72 | 0.3151 |

Reaction conditions: Mass of catalyst, 0.2 g; Reaction temp., 973 K; Reaction pressure, 0.1 MPa; Reaction time, 4 h; Reactant gas, CH₄/CO₂/Ar = 44.0/47.2/8.8, 40 ml min⁻¹. The conversions listed here were the average values during a 4h reaction.

Influence of reduction temperature in 10%Ni/SiO₂ catalysts in the reaction

Table 3 shows the results of the CH₄-CO₂ reforming reaction which was implemented at 973 K and ordinary pressure (0.1 MPa) for 4 h on the 10%Ni/SiO₂ catalysts calcined in air at 773K for 2 h under different reduction temperature of 623 K, 673 K, 723 K, 773 K, 823 K, respectively.

Table 3 shows that the conversion of CH₄, CO₂ and total carbon increased with the reduction temperature rising from 623 K to 723 K, and then decreased when the reduction temperature elevating from 723 K to 823 K with almost opposite tendency of the carbon deposition. Therefore, the reduction temperature of 723 K and the calcination temperature of 773 K for the 10%Ni/SiO₂ catalyst was favorable in the CH₄-CO₂ reforming reaction, and the conversion of CH₄, CO₂ and total carbon of 67.27%, 67.21%, 67.24%, respectively, and the carbon deposition of 0.2698 g were obtained on the 10%Ni/SiO₂.

Table 3 Influence of reduction temperature in 10%Ni/SiO₂ catalysts on the reaction

| R. T. /K | CH ₄ conv./% | CO ₂ conv./% | C _{total} conv./% | carbon deposition/g |
|----------|-------------------------|-------------------------|----------------------------|---------------------|
| 623 | 65.78 | 63.78 | 64.76 | 0.2855 |
| 673 | 66.39 | 65.07 | 65.60 | 0.2835 |
| 723 | 67.27 | 67.21 | 67.24 | 0.2698 |
| 773 | 67.16 | 64.40 | 65.59 | 0.2750 |
| 823 | 65.57 | 64.20 | 64.88 | 0.2987 |

Reaction conditions: Catalyst, 0.2 g; Reaction temp., 973 K; Reaction pressure, 0.1 MPa; Reaction time, 4 h; Reactant gas, CH₄/CO₂/Ar = 44.0/47.2/8.8, 40 ml min⁻¹. The conversions listed here were the average values during 4h reaction.

Influence of Cr₂O₃ promoter loadings in 10%Ni/SiO₂/Cr₂O₃ catalysts on the reaction.

Table 4 shows the results of the CH₄-CO₂ reforming reaction which was implemented at 973 K and ordinary pressure (0.1 MPa) for 4 h on the 10%Ni/SiO₂/Cr₂O₃ catalysts with different Cr₂O₃ loadings, and calcined in air at 773 K for 2 h and reduced in the atmosphere of 99.999% H₂ at 723 K for 2 h at a heating rate of 10 K/min.

Table 4 shows that the conversion of CH₄, CO₂ and total carbon increased when Cr₂O₃ promoter loadings increased from 0.5% to 1.0%, and then decreased with promoter Cr₂O₃ loading increasing from 1.0% to 2.5% roughly. Meanwhile, the carbon deposition decreased with promoter Cr₂O₃ loading increasing from 0.5% to 1.0% and then increased with promoter Cr₂O₃ loading increasing from 1.0% to 2.5%. Therefore, promoter Cr₂O₃ loading of 1.0% in the Ni/SiO₂/Cr₂O₃ catalyst was favorable for the CH₄-CO₂ reforming reaction, and the conversion of CH₄, CO₂ and total carbon of 69.86%, 70.47%, 70.20, respectively, and the carbon deposition of 0.1987g were obtained on the Ni/SiO₂/Cr₂O₃ catalyst. Therefore, the action of the promoter Cr₂O₃ in Ni/SiO₂/Cr₂O₃ catalyst was to decrease the carbon deposition and increase the total carbon conversion.

Table 4 Influence of Cr₂O₃ promoter loadings in 10%Ni/SiO₂ catalysts in the reaction

| promoter loading /% | CH ₄ conv./% | CO ₂ conv./% | C _{total} conv./% | carbon deposition/g |
|---------------------|-------------------------|-------------------------|----------------------------|---------------------|
| 0 | 67.27 | 67.21 | 67.24 | 0.2698 |
| 0.5 | 66.71 | 65.54 | 67.48 | 0.2158 |
| 1 | 69.86 | 70.47 | 70.20 | 0.1987 |
| 1.5 | 70.05 | 69.43 | 69.43 | 0.2189 |
| 2 | 66.44 | 67.83 | 67.83 | 0.2312 |
| 2.5 | 67.70 | 68.44 | 68.44 | 0.2838 |

Reaction conditions: Catalyst, 0.2 g; Reaction temp., 973 K; Reaction pressure, 0.1 MPa; Reaction time, 4 h; Reactant gas, CH₄/CO₂/Ar = 44.0/47.2/8.8, 40 ml min⁻¹. The conversions listed here were the average values during a 4h reaction.

CONCLUSIONS

The CH₄-CO₂ reforming reaction to produce syngas had received considerable attention from both economical and environmental development. However, the main problem in delaying large-scale industrialization is the rapid deactivation of the catalysts caused by carbon deposition and reactive metal sintering. Therefore, a series of catalysts with different Ni loadings, calcination temperature, reduction temperature and Cr₂O₃ promoter loadings were prepared by the method of impregnation for the CH₄-CO₂ reforming reaction. The results of the reactions showed that the best activity and the carbon deposition resistance were obtained on the Ni/SiO₂/Cr₂O₃ catalyst with the Ni loading of 10% and the Cr₂O₃ promoter loading of 1.0%, calcined at 773 K in air for 2 h and reduced at 723 K by H₂ for 2 h in the CH₄-CO₂ reforming reaction. The conversion of CH₄, CO₂ and total carbon achieved 69.86%, 70.47% and 70.20% on the Ni/SiO₂/Cr₂O₃ catalyst in the CH₄-CO₂ reforming

reaction. The carbon deposition on Ni/SiO₂/Cr₂O₃ catalyst was decreased 26.35% compared to that on Ni/SiO₂ catalyst.

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