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Steam Reforming of Methane using Ni-based Monolith Catalyst in Solid Oxide Fuel Cell System

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Abstract

Natural gas is a suitable fuel supply for solid oxide fuel cell (SOFC) system due to its increasingly improved infrastructure and relatively low cost. Natural gas should be reformed to syngas before it is introduced to SOFC system. Reforming catalyst is one of the key techniques in steaming reforming of natural gas. Compared with pellet catalyst, monolith catalyst can reduce the pressure drop and temperature gradient in the reformer. This work focuses on monolith catalyst and its usage in the reformer.

In this work, Ni-based monolith catalyst (modified by Mg) was prepared and tested in steam reforming of methane. When the water to methane ratio is 3, the conversion of methane reaches 99% at 800°C with the gas hourly space velocity (GHSV) is 3000 h^{-1}. Percentage of hydrogen in the reforming product gases is about 75% and the performance of this catalyst is stable. The interaction between Ni and support was analyzed using temperature-programmed reduction (TPR) technique and the results showed that NiO-MgO solid solution can strengthen the interaction between Ni and support so that the anti-carbon disposition ability and stability of the catalyst was improved.

Methane steam reformer testing equipment with the processing capability of 7 SLM CH_4 was established and it can meet the demand of 1~2 kW SOFC system. The hydrogen production of this reformer reaches 22.7 SLM and the conversion of CH_4 is 97.8%.

Introduction

Solid oxide fuel cell (SOFC) will play an important role in clean energy field due to their high efficiency and non-pollution and it is paid more and more attention. Natural gas is an appropriate fuel supply for SOFC system because of its widespread infrastructure and relatively low cost. Steam reforming is an effective method to convert natural gas into hydrogen and the catalyst is necessary in this reaction.

Monolith catalyst [1,2] has some advantages such as low pressure drop and low temperature gradient. These advantages of monolith catalyst make it suitable for SOFC reformer. This work investigates the performance of monolith in steam reforming of methane and various methods such as X-ray diffraction (XRD), thermo gravimetric (TG) and temperature programmed reduction (TPR) were used to analyze the catalyst.

1. Experimental

1.1 Catalyst preparation

The honeycomb cordierite with a cell density of 400 cells per inch was purchased and tailored to a suitable size. The cordierite support was firstly coated by Al_2O_3 and after this process, the active component Ni was coated on cordierite support by wet impregnation method using $Ni(NO_3)_2 \cdot 6H_2O$ as a precursor. MgO was introduced into the catalyst by wet impregnation method. The cordierite impregnated with $Ni(NO_3)_2 \cdot 6H_2O$ was then dried for 12 h at 110°C and was calcined for 4 h at 600~800°C.

1.2 Catalyst performance test

The prepared catalyst was tested using fixed bed reactor equipment. Before steam reforming reaction, the catalyst was reduced by hydrogen at 800°C. The gas products were analyzed by gas chromatography equipped with a Thermal Conductivity Detector (TCD). The performance of the monolith catalyst was evaluated at different temperature, different steam/carbon ratios and different gas hourly space velocity (GHSV). The prepared monolith catalyst and test equipment were shown in Fig.1.
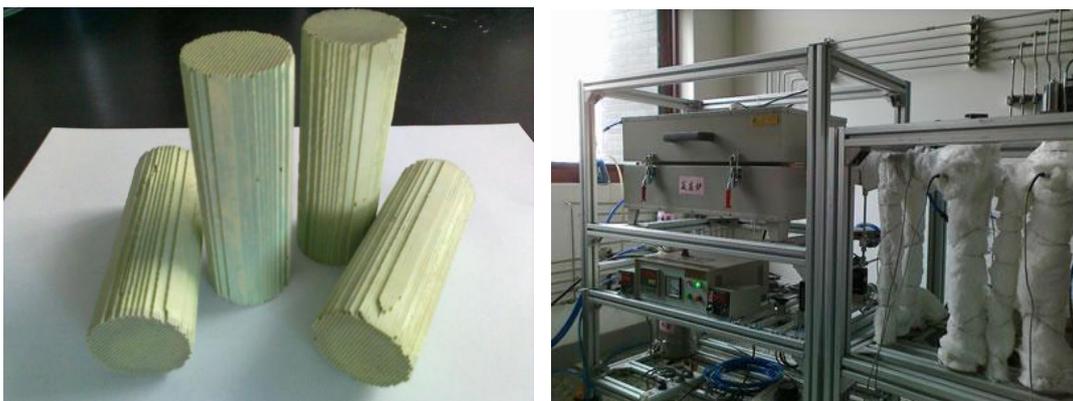

Fig.1 Monolith catalyst (left) and fixed bed reactor equipment (right)

1.3 Catalyst characterization

The morphologies of the monolith catalyst were determined by X-ray diffraction (XRD) method. XRD patterns were obtained in D8 Discover (Bruker, AXS) equipment using Cu*Kα*

radiation at 40 kV and 40 mA. The carbon deposition of the recovery catalyst after reaction was determined using thermogravimetric (TG) method.

1.4 Temperature programmed reduction (TPR) test

The reducibility of the monolith catalyst was detected via H_2-Temperature programmed reduction (H_2-TPR) method. Before this test, the catalyst was treated in N_2 at 300°C for 0.5h, and then cooled to 50°C. After this, the mixed gas (10%H_2+90%Ar) was introduced into the reactor and at the same time, temperature was raised until to 900°C at 5°C /min. The data was collected by control software. TPR process is shown in Fig.2.
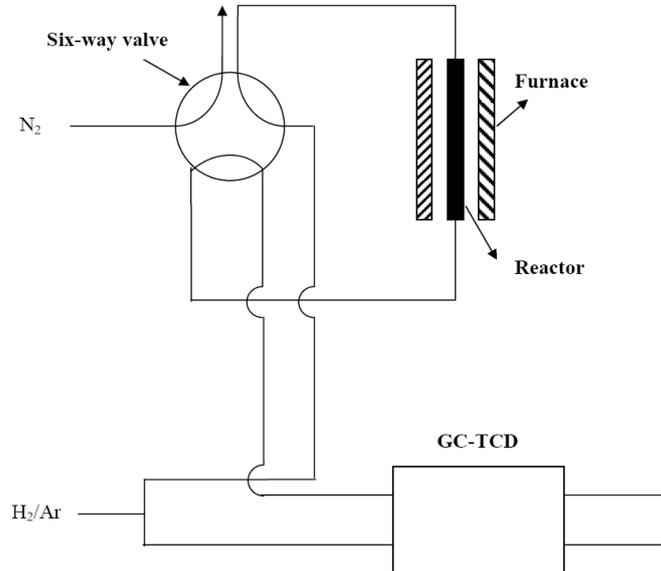

Fig.2 Schematic diagram of TPR test

2. Results and discussion

2.1 X-ray result of the monolith catalyst

The XRD analysis result was shown in Fig.3. NiO phase was found and it is the active specie. Cordierite mainly contains MgO, Al_2O_3 and SiO_2.
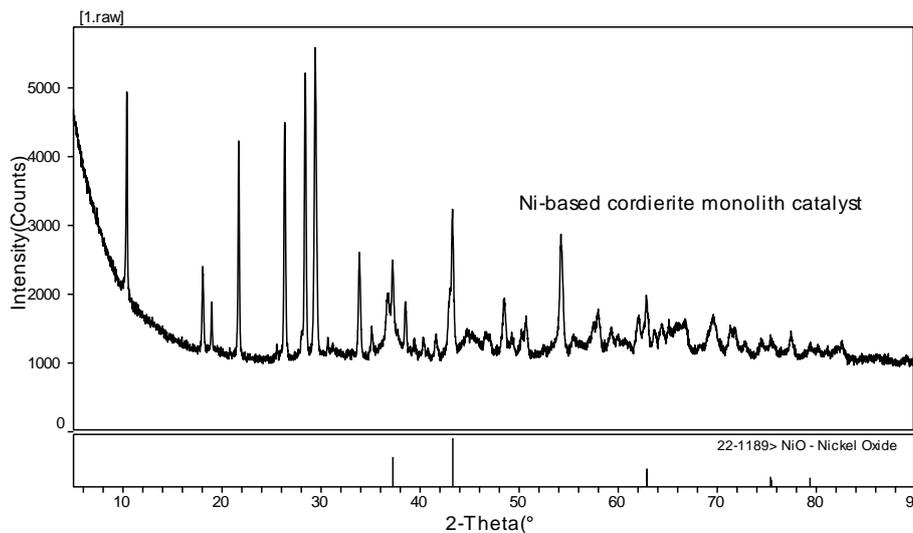

Fig.3 XRD analysis of the monolith catalyst

2.2 Reforming performance of the monolith catalyst

The prepared monolith catalysts are cylindrical and two types of samples with different diameter (12mm and 30mm) were used to catalyze steam reforming of methane. The 12mm catalyst was tested in quartz reactor and the 30mm catalyst was tested in a steel reactor.

The performance of monolith catalyst in steam reforming of methane at different temperature is shown in Table 1. The conversion of methane increases with the increase of GHSV. High temperature facilitates steam reforming of methane because this reaction is endothermic.

Table 1 Performance of Ni-based monolith catalyst at different reaction temperature

Temperature °C	Gas products (V%)				Conversion of CH_4	Selection of CO
	H_2	CO	CO_2	CH_4		
700	72.1%	10.3%	10.9%	6.6%	76.4%	48.6%
750	74.5%	13.5%	9.4%	2.7%	89.5%	58.9%
800	76.0%	16.9%	6.9%	0.13%	99.5%	70.9%

∗ The GHSV is 3000 h^{-1}.

Table 2 listed the performance of monolith catalyst in steam reforming at different steam/carbon ratios. In these tests, GHSV keeps consistent and the value is 2000 h^{-1}. The conversion of methane increases with the increase of steam/carbon ratio. Conversion of methane approaches 100% approximately when the steam/carbon ratio is 3, compared 83.3% while the steam/carbon ratio is 1. It proved that increase of steam material facilitates steam reforming reaction. On the other hand, relative amount of CO increases with the decrease of steam/carbon ratio. The percentage of CO reaches 24.2% while the steam/carbon ratio is 1. Equation (1) and Equation (2) listed the main reaction equations in steam reforming of methane. When reaction is processing at higher steam/carbon ratio such as S/C is 3, Equation (2) is prevailing over Equation (1) so that the relative amount of CO_2 is increased. On the contrary, When reaction is processing at lower steam/carbon ratio such as S/C is 1, Equation (1) is prevailing over Equation (2) so that more CO is produced. In a word, the selection of either CO or CO_2 is determined by steam/carbon ratio. From Table 2, it can be seen that H_2 is the main component in the gas products and its relative volume always accounts for over 70% when steam/carbon changes from 1 to 3.

$$CH_4 + H_2O \rightarrow 3H_2 + CO, \Delta_r H_m^\theta (298.15K) = 206kJ/mol \tag{1}$$

$$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2, \Delta_r H_m^\theta (298.15K) = 165kJ/mol \tag{2}$$
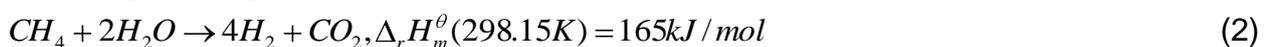
Table 2   Reforming performance of Ni-based monolith catalyst at different steam/carbon ratios

Steam/carbon ratio	Gas products (V%)				Conversion of CH$_4$	Selection of CO
	H$_2$	CO	CO$_2$	CH$_4$		
S/C=1	70.9%	24.2%	∼0	4.8%	83.3%	∼1
S/C=2	74.8%	20.4%	4.2%	0.5%	97.7%	82.9%
S/C=3	75.9%	17.9%	6.2%	∼0	∼1	74.2%

＊ Reaction temperature is 800℃, GHSV=2000 h^{-1}.

Table 3 displayed the performance of monolith catalyst in steam reforming at different GHSV. The conversion of methane decreases with the increase of GHSV. When the GHSV increases from 2000 h^{-1} to 5000 h^{-1}, the conversion of methane decreases from about 100% to 90.7%. Correspondingly, the conversion of CO decreases from 17.9% to 14.7% while the conversion of CO$_2$ increases from 6.2% to 8.6%. It indicates that when reaction is processing at higher GHSV such as GHSV is 5000 h^{-1}, Equation (2) is prevailing over Equation (1) so that the relative amount of CO decreases while the relative amount of CO$_2$ increases. That is to say, the selection of CO decreases with the increase of GHSV.

Table 3 Performance of Ni-based monolith catalyst at different GHSV

GHSV (h^{-1})	Gas products (V%)				Conversion of CH$_4$	Selection of CO
	H$_2$	CO	CO$_2$	CH$_4$		
2000	75.9%	17.9%	6.2%	∼0	∼1	74.2%
3000	76.0%	16.9%	6.9%	0.13%	99.5%	70.9%
4000	75.1%	15.3%	8.3%	1.3%	94.8%	64.8%
5000	74.3%	14.7%	8.6%	2.3%	90.7%	63.0%

＊ The reaction temperature is 800°C and the steam/carbon (S/C) ratio is 3.

The aim of developing the monolith catalyst is to apply it in SOFC system. So besides testing this catalyst in micro-reactor equipment, the catalyst with bigger diameter (30 mm) is also evaluated in steel reactor equipment (reformer). The result reveals that in one of self-designed reformers, when the methane feed is 7 SLM, the conversion of CH$_4$ is 97.8% and the produced hydrogen reaches 22.7 SLM and it can meet the demand of 1~2kW SOFC system.

2.3 TG analysis of recovered the monolith catalyst after reaction
A monolith catalyst was recovered after 6 days reaction and TG analysis method was used to evaluate carbon deposition of the catalyst and the result was revealed in Fig.4. The calculated relative amount of carbon deposition is 5.67% (weight). Carbon deposition has adverse effect on performance of catalyst. Some methods such as enhancing catalyst structure and increasing steam/carbon ratio can lessen carbon deposition.
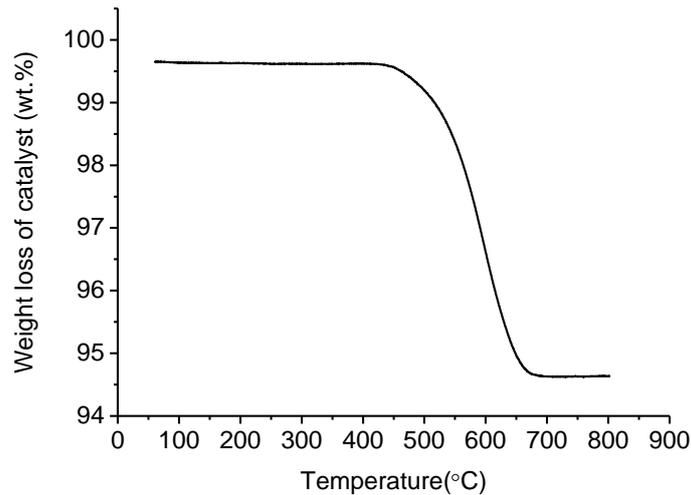
Fig.4 TG analysis of the recovered catalyst after reaction

Carbon deposition of the catalyst used in the reformer should be watched. If conversion of methane decreases apparently it indicates that activation of the catalyst may possibly decrease due to carbon deposition. One of the effective methods to remove carbon deposition is to let the steam reforming reaction run at higher steam/carbon ratio. Increase of steam feed is helpful to convert carbon into either CO or CO_2 as the Equation (3) and Equation (4) describe.

$$C + H_2O \rightarrow CO + H_2, \Delta_r H_m^\theta(298.15K) = 131 kJ/mol \tag{3}$$
$$C + 2H_2O \rightarrow CO_2 + 2H_2, \Delta_r H_m^\theta(298.15K) = 89 kJ/mol \tag{4}$$
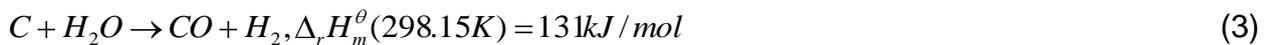
2.4 TPR analysis of Ni-based monolith catalyst
The reducibility of the Ni-based monolith catalysts calcined at different temperature was determined by H_2-TPR method and the results were shown in Fig.5. It can be seen that there were 3 reduction peaks for the two catalysts and correspondingly, there are three Ni species in the two catalysts. Corresponding to reduction peaks, the Ni species[3] are free NiO, dispersed NiO and fixed NiO from low temperature to high temperature, respectively. The reduction peak moved toward the higher temperature with the increase of the calcined temperature of the catalyst. It revealed that the interaction between Ni component and the support increases with the increase of temperature of the reduction. NiO-MgO solid solution[4] can strengthen the interaction between Ni and support to improve stability of the catalyst.
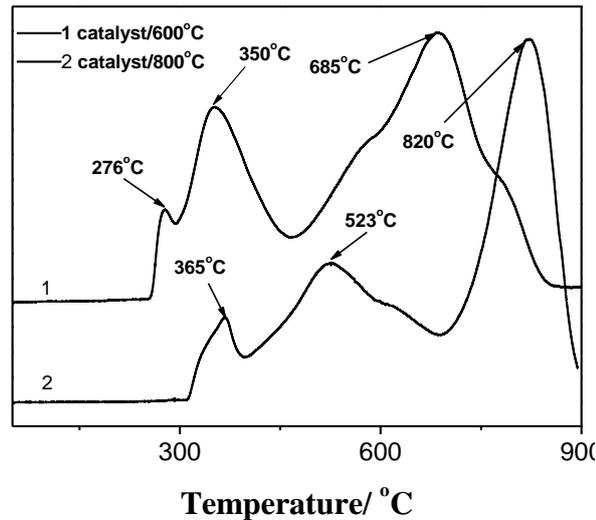
Fig.5 TPR patterns of Ni-based monolith catalyst

3. Summary

Ni-based monolith catalyst was prepared and used in steam reforming of methane. XRD method was employed to analyze the active species in the catalyst. The performance of the monolith catalyst was evaluated at different temperature, different steam/carbon ratios and different GHSV. Carbon deposition of catalyst was determined by TG method and the reducibility of catalyst was examined by TPR method.

Conversion of methane increases with the increase of reaction temperature and steam/carbon ratio. When the steam/carbon ratio is 3, the conversion of methane reaches 99% at 800°C with the GHSV is 3000 h^{-1}. Percentage of hydrogen in the reforming product gases is about 75% and the performance of this catalyst is stable. Conversion of methane decreases with the increase of GHSV. TPR results revealed that NiO-MgO solid solution can strengthen the interaction between Ni and support so that the anti-carbon disposition ability and stability of the catalyst was improved.

The produced hydrogen of one of self-designed reformers in which the Ni-based monolith catalyst was used reaches 22.7 SLM and the conversion of CH_4 is 97.8% and the processing capacity of this reformer can meet the demand of 1~2kW SOFC system.

Acknowledgement

References

[1]   Pingyi Wu, Xiujin Li , Shengfu Ji,Bao Lang, Fabien Habimana, Chengyue Li. Steam reforming of methane to hydrogen over Ni-based metal monolith catalysts. Catalysis Today, 2009,146(1-2):82-86.

[2]   Jae Hong Ryu, Kwan Young Lee, Hak Joo Kim b, Jung-Il Yang, Heon Jung. Promotion of palladium-based catalysts on metal monolith for partial oxidation of methane to syngas. Applied Catalysis B: Environmental, 2008,80(3-4):306-312.

[3]   N. Sahli, C. Petit, A.C. Roger, A. Kiennemann, S. Libs, M.M. Bettahar. Ni catalysts from $NiAl_2O_4$ spinel for CO_2 reforming of methane. Catalysis Today, 2006,113(3-4):187-193.

[4]   Chenguang Wang, Tiejun Wang, Longlong Ma, Yan Gao, Chuangzhi Wu. Steam reforming of biomass raw fuel gas over NiO–MgO solid solution cordierite monolith catalyst. Energy Conversion and Management, 2010, 51(3):446-451.