

Partial oxidation reforming of biomass fuel gas over nickel-based monolithic catalyst with naphthalene as model compound

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Abstract—With naphthalene as biomass tar model compound, partial oxidation reforming (with addition of O₂) and dry reforming of biomass fuel gas were investigated over nickel-based monoliths at the same conditions. The results showed that both processes had excellent performance in upgrading biomass raw fuel gas. Above 99% of naphthalene was converted into synthesis gases (H₂+CO). About 2.8 wt% of coke deposition was detected on the catalyst surface for dry reforming process at 750 °C during 108 h lifetime test. However, no coke deposition was detected for partial oxidation reforming process, which indicated that addition of O₂ can effectively prohibit the coke formation. O₂ can also increase the CH₄ conversion and H₂/CO ratio of the producer gas. The average conversion of CH₄ in dry and partial oxidation reforming process was 92% and 95%, respectively. The average H₂/CO ratio increased from 0.95 to 1.1 with the addition of O₂, which was suitable to be used as synthesis gas for dimethyl ether (DME) synthesis.

Key words: Biomass Fuel Gas, Monolithic Catalyst, Partial Oxidation Reforming, Tar Elimination

INTRODUCTION

The use of biomass fuel gas is attracting more and more attention nowadays. The main components of biomass fuel gas produced from biomass gasification are H₂, CO, CO₂, CH₄, tar and other light hydrocarbons [1]. The upgrading of biomass fuel gas to syngas is a very important process to the utilization of biomass, because syngas is the building block for many chemicals just like methanol, dimethyl ether and higher hydrocarbons through the Fischer-Tropsch process. Up to now, syngas has been mainly produced by steam reforming of natural gas in industry:



This reaction is endothermic, so it is necessary to supply heat. At a pressure between 1.5 and 3.0 MPa over Ni/ α -Al₂O₃ catalysts, the reaction temperature has to be kept around 900 °C. In order to reduce the energy consumption, partial oxidation of methane has been extensively studied [2-4]. Researchers have investigated various reaction conditions, and high yields of syngas have been reported [5-11].

Recently, more and more researchers have been paying attention to the use of monolithic catalysts for conversion of methane. Different kinds of monoliths have been used and show good performance on methane conversion and natural gas utilization. Corella's group made nickel-based monoliths and used on hot gas steam reforming in biomass gasification in fluidized beds [12-14]. The use of monoliths has attracted more attention from VTT in Finland and the Fraunhofer UMSICHT Institute in Oberhausen, Germany. Compared with a fix-bed reactor and slurry reactor, using monolithic catalysts has several advantages: high catalytic performance per unit mass of active metal, high operating stability and low pressure drop

of catalyst bed [15-19].

We prepared high stable nickel catalysts and tested their characterization and performance of reforming biomass fuel gas [21,22]. The catalyst exhibited excellent performance. However, due to the atmospheric biomass gasifier, the high temperature raw fuel gas from gasifier cannot flow through a reforming catalyst bed that has a high pressure drop.

In this paper, nickel monolithic catalysts were prepared by wet impregnation of NiO on the surface of cordierite. The performance of dry reforming and partial oxidation reforming of biomass fuel gas was investigated over nickel monolithic catalysts. The catalyst characterization was also made by method of thermogravimetry.

EXPERIMENTAL

1. Preparation of the Catalysts

The nickel monolithic catalysts were prepared by wet impregnation of NiO on cordierite support whose surface area was increased by wet impregnation of γ -Al₂O₃ superfine powder. The prepared method was as follows. The cordierite was first etched in 30 wt% oxalic acid solution under vacuum for 30 minutes and then the water evaporated. After being washed by distilled water, the support was dried overnight at 120 °C. The surface area of the cordierite support was increased by wet impregnation with superfine γ -Al₂O₃ powder ethanol solution. After drying overnight at 120 °C, the support was calcined at 750 °C for 10 h. The process was repeated for three times, then the support was impregnated with nickel nitrate solution (72.38 g Ni(NO₃)₂ and 200 ml distilled water) for 24 hours. The catalyst was dried at 110 °C overnight and calcined at 800 °C. The catalyst was designated as MC-3. Physical characteristics and chemical composition of catalyst MC-3 are listed in Table 1.

2. Characterization

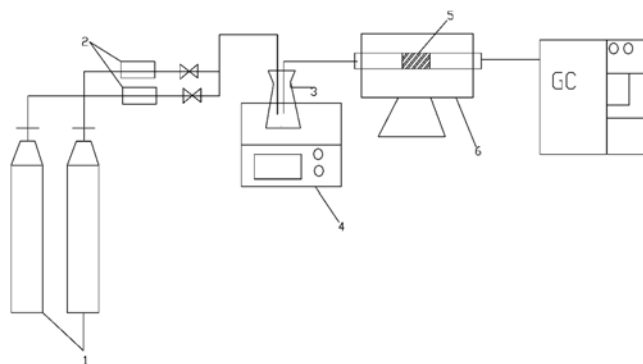
The crystal structure of the catalysts before and after reaction was

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Table 1. Physical characteristic and chemical composition of catalyst MC-3

catalyst dimension/mm				NiO /wt%	Al ₂ O ₃ /wt%
Length	Outer diameter	Hole diameter	Wall thickness		
50	40	1	1	3.74	3.81

**Fig. 1. Schematic diagram of the reforming experiment.**

- | | |
|-------------------------|---------------|
| 1. Gas | 4. Water-bath |
| 2. Mass flow controller | 5. Catalyst |
| 3. Tar pot | 6. Furnace |

determined by X-ray powder diffraction (XRD) in a Rigaku D/max-III B apparatus by using CuK α radiation, at 40 kv and 30 mA. Diffraction peaks recorded in a 2θ range between 5° and 80° were used to identify the structure of the samples.

TG-DTG studies of used catalysts powder were carried out under an oxidative atmosphere with analyzers by using 10–15 mg of sample and a $10^\circ\text{C}/\text{min}$ temperature increasing rate.

3. Catalytic Reforming Reaction

A schematic diagram of the reforming system is shown in Fig. 1. The reactor was composed of an electric furnace and a quartz tube (outer diameter: 45 mm, wall thickness: 2 mm). The gap between the monolithic catalyst and reactor wall was sealed with quartz fiber.

The composition of the biomass fuel gas was H₂: 16.04 vol%, CO: 12.10 vol%, C₂H₄: 2.50 vol%, CO₂: 21.95 vol%, CH₄: 15.08 vol%, N₂: 32.33 vol%. The reforming reactor was atmospheric and temperature was kept at 750°C . Naphthalene was added in the biomass fuel gas as the tar model compound to study the performance of tar elimination. For all runs, the flow rate of biomass fuel gas was 300 sccm. In the partial oxidation reforming runs, additional 60 sccm of mixed gas (O₂/N₂=95/5, mol/mol) was added into the reactor to investigate the promotion effect of oxygen addition.

First, the catalysts were reduced by mixed gas (H₂/N₂=5/95, mol/mol) with flow rate of 300 sccm from room temperature to 750°C within 2 h. Then reactant gases were fed into the reactor. After reforming runs were over, the pure N₂ was fed into the reactor to cool the reactor temperature to room temperature and the catalyst was taken out for coke deposition analysis. The composition of dry producer gases was analyzed by gas chromatograph (GC) and gas chromatogram-mass spectrum (GC-MS) after sampling.

4. Outlet Gas Analysis System

The contents of N₂, CO, CO₂, CH₄, H₂ in outlet gas were analyzed

with a gas chromatograph (model GC-9800, Shanghai Kechuang Corp., China) equipped with a thermal conductivity detector (TCD). The column was TDX-01 and carrier gas was He. The contents of CH₄, C₂H₄ were analyzed with another GC-9800 gas chromatograph equipped with a flame ionization detector. The column was Porapak Q and carrier gas was N₂.

The products of tar cracking were analyzed by GC/MS (Agilent, Hp-1). The preconcentrator, GC and MS are Entech 7100, Agilent 6890, Agilent 6973, respectively.

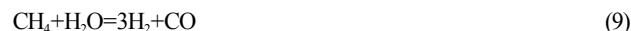
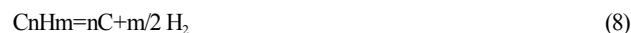
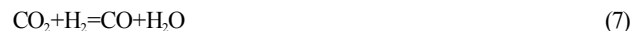
RESULTS AND DISCUSSION

1. Reforming Reaction

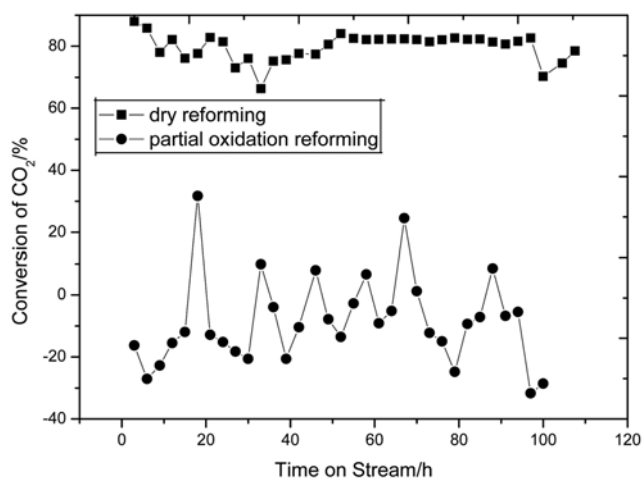
In the partial oxidation reforming runs, the oxidation of biomass fuel gas occurred first when reactants were fed into the reactor. The main oxidation reactions are shown as below [23]:



Then reforming reactions occurred over monolithic nickel catalyst. The main reforming reactions are shown as below:



At the desired reforming temperature, all of reactions mentioned above reached chemical equilibrium and determined the composition of outlet gas. Because reforming reactions are endothermic, high

**Fig. 2. CO₂ conversion vs. time on stream in partial oxidation and dry reformings.**

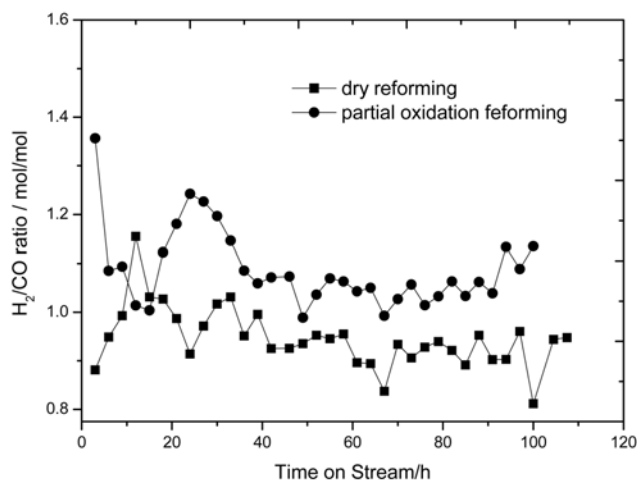


Fig. 3. H₂/CO ratio vs. time on stream in partial oxidation and dry reforming.

reforming temperature is suitable for the tar conversion.

The conversion of CO₂ in dry reforming runs and partial oxidation reforming runs is shown in Fig. 2. The average conversion of CO₂ was 80% in the dry reforming runs. However, the addition of O₂ decreased the conversion of CO₂ sharply due to the oxidation of CO and partial oxidation of CH₄.

The H₂/CO ratio of outlet gas is shown in Fig. 3. In dry reforming runs, the H₂/CO ratio varied between 0.95 and 1.15. In partial oxidation reforming runs, the average H₂/CO ratio varied between 1.09 and 1.35. It indicated that addition of O₂ could increase the H₂/CO ratio of outlet gas. The reasons may be that O₂ reacted with CH₄ and H₂ in biomass fuel gas to produce H₂O, which promoted the water gas shift reaction to increase the H₂/CO ratio. So the composition of outlet gas can meet the requirements of the liquid fuels synthesis process.

In both dry reforming runs and partial oxidation reforming runs, C₂H₄ was not detected in the outlet gas, which means it was converted completely.

2. The Effect of GHSV (Gas Hourly Space Velocity)

Nowadays, it is still difficult to test the tar content in syngas rapidly. However, CH₄ conversion has the same trend with the conversion of tar, so we can use the online test of CH₄ conversion to indicate the effect of GHSV on the tar elimination. With the GHSV increase, not only the conversion of CH₄ decreased, but also the conversion of naphthalene decreased. A tiny amount of smoke appeared at the reactor outlet when GHSV increased to 11,894 h⁻¹. With the GHSV increase further, the smoke became thicker and thicker. CH₄ is more stable than other hydrocarbons, so its conversion is more difficult than that of naphthalene. When the conversion of CH₄ decreased, the conversion of naphthalene decreased too.

The effect of GHSV on the conversion of CH₄ is shown in Fig. 4. The conversion of CH₄ decreased slowly from 56.24% to 52.9% with the GHSV increase from 4,250 h⁻¹ to 8,495 h⁻¹. Then it decreased sharply from 47% to 25% with the GHSV increase from 10,088 h⁻¹ to 25,487 h⁻¹. It indicated that molecular diffusion controlled the reforming reaction.

The H₂/CO ratio variation with the GHSV is shown in Fig. 5. With the GHSV increase from 4,250 h⁻¹ to 25,487 h⁻¹, the H₂/CO

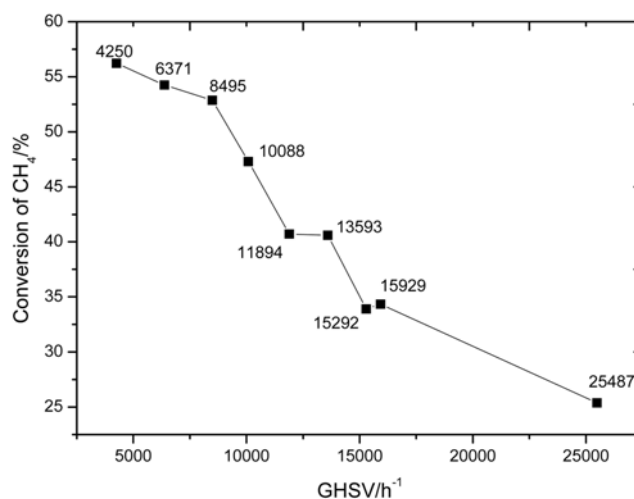


Fig. 4. GHSV vs. conversion of CH₄ in dry reforming.

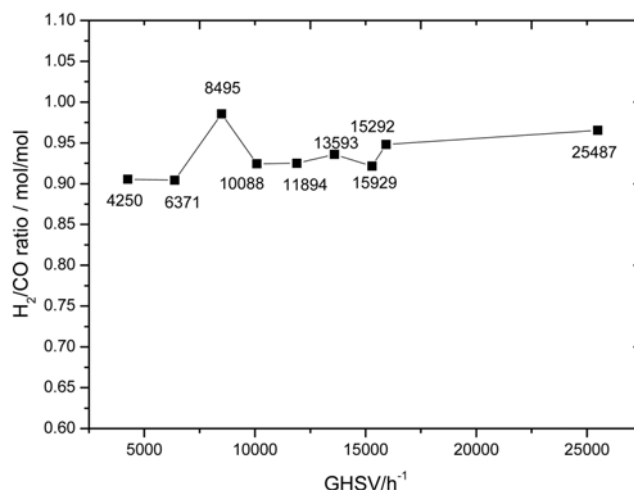


Fig. 5. GHSV vs. H₂/CO of outlet gas in dry reforming.

ratio increased from 0.91 to 0.97. The water gas shift reaction is a fast reaction. So with the GHSV increase, the reforming reaction could not keep equilibrium, but the water gas shift reaction was fast enough to keep equilibrium, which resulted in the H₂/CO ratio increase. Especially when GHSV raised to 8,495 h⁻¹, the two reactions reached the balance point, and the H₂/CO ratio reached its highest point.

3. Biomass Tar Cracking

8.28 g naphthalene as tar model compound was filled in the tar pot (shown in Fig. 1) to investigate the mechanism of the tar cracking on MC-3 monolithic catalyst. The resultants produced by tar cracking were analyzed by GC/MS.

The content of naphthalene in biomass fuel gas was 4.26 g/m³. After partial oxidation reforming over MC-3 catalyst, above 99% of naphthalene was converted to permanent gases such as H₂/CO and lighter components. Corella reported that the tar conversion rate of his monoliths in real fuel gas cleaning ranged from 21% to 96% depending on different operation conditions [10,16]. Our operation condition is cleaner than real fuel gas condition, so the conversion rate is higher.

Table 2. The content of tar species in the outlet fuel gas over MC-3 catalyst

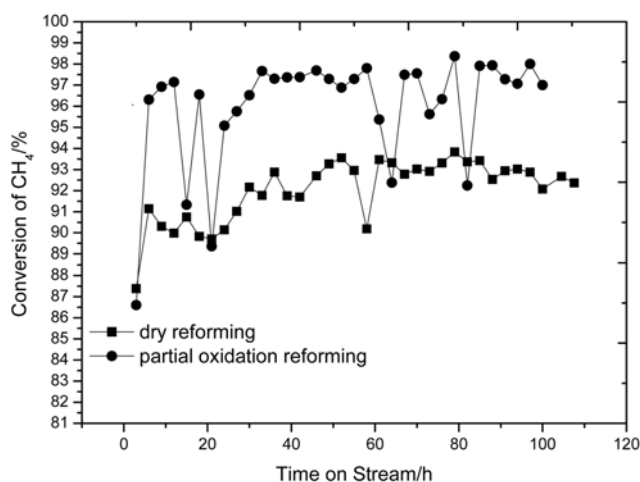
Matter	Residue time (min)	Concentration ($\mu\text{g}/\text{m}^3$)
Butylene	4.76	151.37
Benzene	8.87	276.19
Toluene	11.78	35.33
Ethylbenzene	14.74	8.90
m-Xylene	14.99	9.20
p-Xylene	15.72	5.04
4,7-Dimethyl hendecane	20.79	10.04
3,6-Dimethyl decane	20.95	7.56
3,7-Dimethyl hendecane	21.96	6.26
5-Methyl hendecane	22.1	8.63
Tridecane	26.54	5.35

As shown in Table 2, the concentration of lighter components in outlet gas stream is below $500 \mu\text{g}/\text{m}^3$, which indicates that partial oxidation reforming over MC-3 catalyst shows good performance on tar elimination.

The mechanism of tar cracking may be as follows. The tar molecular absorbed on the surface of the catalyst, then formed a series of media compounds. Some are active species, and others are inert species. CO_2 in biomass fuel gas absorbed on the surface of catalyst, and divided to form CO and O free radicals. CO desorbed from the catalyst surface, and O free radical attacked the media compounds. As shown in Table 2, butylene, benzene and styrene are the main components. The phenomenon may be explained as follows. Naphthalene molecule has different C-C bonds. When O free radical attacks the molecule, the longer bonds like II, IV bonds are easier to rupture and form species like butylene, benzene and styrene. The inert species formed coke via dehydrogenation. I, III bonds are shorter and more difficult to rupture, so the species just like hendecane and decane are less in the outlet gas.

3. Characterization of Catalyst Stability

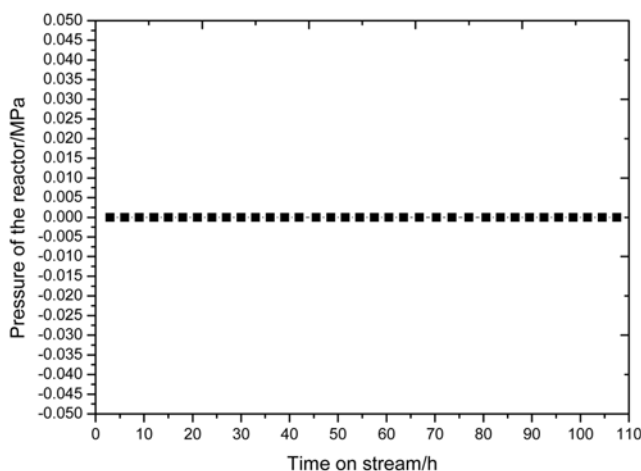
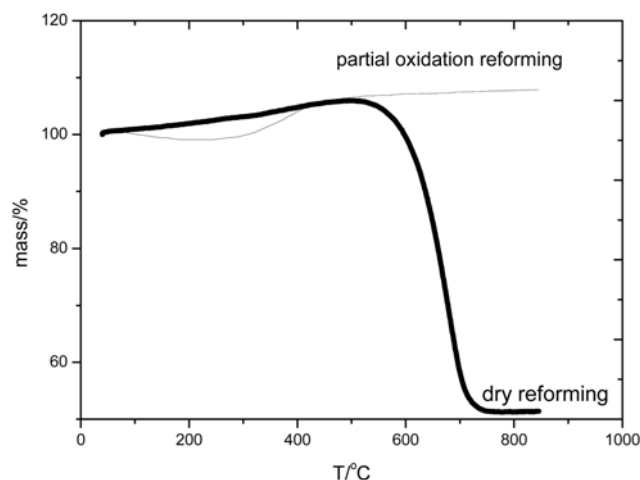
A large amount of CH_4 and CO in biomass fuel gas can result in carbon deposition on the surface of MC-3 catalyst by methane de-

**Fig. 7. CH_4 conversion vs. time on stream in both partial oxidation and dry reforming.**

composition and CO disproportionation side reactions. The tar in the biomass fuel gas would make the carbon deposition more serious. Carbon deposition can cover the surface of the catalysts, reduce the catalysts' activity and even block the reactor. The pressure variation of reactor in partial oxidation reforming runs is shown in Fig. 6. No evident pressure variation was observed, which indicated the merits of the monoliths catalysts.

The results of a lifetime test are shown in Fig 7. The average conversion of CH_4 was 92% in dry reforming process. However, the average conversion of CH_4 was 95.4% in the partial oxidation reforming process. This indicated that the partial oxidation reforming process had higher performance of upgrading biomass fuel gas than dry reforming process. For both processes, no drop of the conversion of CH_4 was observed, which indicated that the MC-3 catalyst had excellent reforming activity and stability. The curve of partial oxidation changes sharply was caused by the asymmetry of the mixture of O_2 and fuel gas.

The amount of carbon deposited on the MC-3 catalysts was investigated by measuring the catalyst weight variation after the used catalysts were calcined from room temperature to 900°C and kept

**Fig. 6. Pressure as functions of time on stream.****Fig. 8. TG curves of the coke sample on the used catalysts.**

for 2 hours in atmosphere. No evident carbon deposition was detected on the used MC-3 catalyst for partial oxidation reforming process. However, the carbon deposition was 2.78 wt% for dry reforming process.

We collected coke samples from the surface of MC-3 catalyst to investigate the characteristics of carbon deposition by thermogravimetry. The TG curves of the used catalysts are shown in Fig. 8. The evident weight loss of catalyst for dry reforming process can be observed from 500 °C to 700 °C. It is the γ -C (peak temperature: 600 °C) covering on the surface of catalyst. For the catalyst of partial oxidation reforming process, a little weight loss was observed from 100 °C to 260 °C. It is the α -C (peak temperature: 200 °C), which is more active than γ -C. So it is easier to remove by oxidation. The raised peak was observed from 290 °C to 460 °C, which may be caused by the oxidation of Ni atom on the surface of MC-3 catalyst.

The DSC and TG curves of used catalyst for partial oxidation reforming process are shown in Fig. 9. The first exothermic peak appeared between 260 °C and 280 °C, which shows the oxidation of the α -C deposited on the monolithic catalyst. The second exothermic peak appeared at 400 °C, which shows the oxidation of Ni atom on the surface of the catalyst.

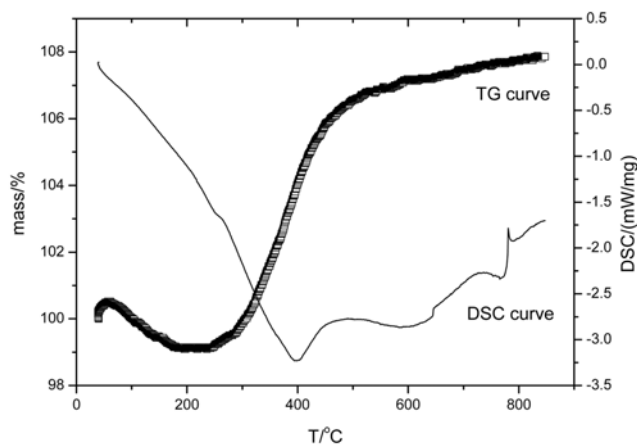


Fig. 9. TG and DSC curves of the coke sample on the used catalyst (partial oxidation reforming).

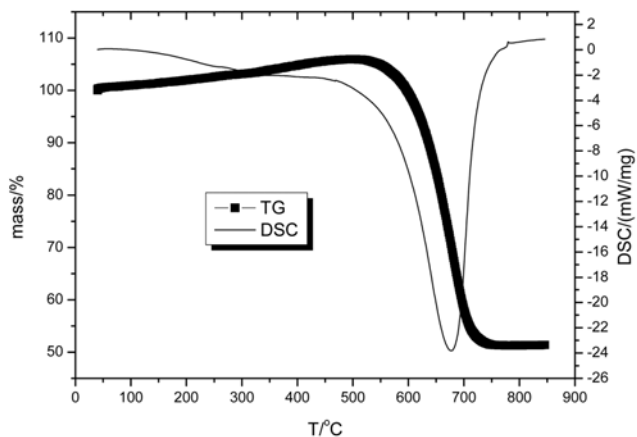


Fig. 10. TG and DSC curves of the coke sample on the used catalyst (dry reforming).

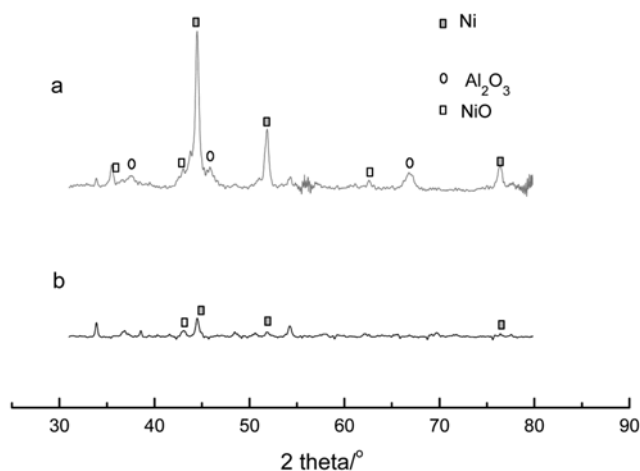


Fig. 11. XRD patterns of MC-3 catalysts (a) after 108 h dry reforming (b) reduced catalyst in 923 K.

The DSC and TG curves of used catalyst for dry reforming process are shown in Fig. 10. Two exothermic peaks appeared at 260 °C and 500 °C respectively, which shows the α -C and γ -C. Like the results shown in Fig. 8 and Fig. 9 α -C is less than γ -C, which shows that carbon deposition in dry reforming is heavier than that in partial oxidation reforming. The results mentioned above indicated that the addition of O₂ could reduce the carbon deposit on the MC-3 catalyst effectively.

Fig. 11 shows the XRD patterns obtained over the catalyst. The results show that Ni exists in the reduced and used catalysts. This means that the sintering of nickel cluster occurred under the reaction conditions. The peaks at 44.6°, 51.9° and 76.4° were identified as Ni metal, the intensities of these peaks in reduced catalyst are weak, which means the Ni atoms had formed a highly dispersed active phase and a large active surface area as bound-state Ni species after pre-reduction. The intensities of the peaks assigned to Ni increased after reaction. This means the sintering of nickel cluster. Sintering is an important reason for the deactivation of Ni-based catalyst. But the catalyst did not induce any deactivation after 108 h dry reforming, because of the high dispersion and thus for the sintering-resistant behavior of the catalyst. NiO and Al₂O₃ were also found in the used catalyst, which may have been caused by the weakening of the effect between nickel atoms and the supports and the oxidation of Ni atoms.

CONCLUSIONS

MC-3 monolithic catalysts showed excellent reforming activity for both dry reforming process and partial oxidation reforming process. Above 99% of naphthalene in the feedstock was converted into synthesis gases (H₂+CO). Only trace lighter hydrocarbons (<10 mg/Nm³) as aerosol remained in the producer gases. The average conversion of CH₄ reached 90% and the H₂/CO ratio of outlet gas approached to 1.0. The addition of O₂ for partial oxidation reforming increased the H₂/CO ratio of outlet gas and the conversion of CH₄ effectively. With GHSV increase, the conversion of CH₄ and tar decreased, but the H₂/CO ratio increased.

No pressure drop of reactor was detected during the 108 h life-

time test for both dry reforming and partial oxidation reforming runs. The conversion of CH_4 and H_2/CO ratio of outlet gas remained stable. MC-3 monolithic catalysts showed excellent stability. The partial oxidation reforming reduced the carbon deposition on the monolithic catalyst effectively.

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