



## Steam reforming of biomass raw fuel gas over NiO–MgO solid solution cordierite monolith catalyst

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### ABSTRACT

The NiO–MgO solid solution cordierite monolith catalyst was prepared by impregnation. 60 h steam reforming tests were carried out at 1023 K. TG was used to analyze the carbon deposition on the catalyst. GC and GC–MS were used to analyze the component of biomass fuel gas and tar. The results show that steam reforming can effectively improve the quality of fuel gas, H<sub>2</sub>/CO ratio can be adjusted by steam reforming. The addition of steam can also increase the activity and stability of the catalyst dramatically. The CH<sub>4</sub> conversion reached 94%. TG shows that the addition of steam can decrease the carbon deposition on the catalyst. GC–MS result shows that most of the tar was converted to H<sub>2</sub>, CO and trace lighter component. Steam reforming can eliminate the biomass tar species more deeply than dry reforming.

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### 0. Introduction

Biomass is an abundantly available and renewable energy resource. Conversion of biomass to synthesis gas and hydrogen contributes to the environmental protection by the decrease of CO<sub>2</sub> emission [1]. Gasification is currently a leading option for converting biomass to synthesis gas technology. Before use as fuel or chemical synthesis, raw fuel gas from biomass gasification has to be purified [2,3]. This is because the conversion of synthesis gas to clean liquid fuels, such as DME and Fischer–Tropsch oil needs clean gas. The high content of tar and low H<sub>2</sub>/CO ratio in biomass fuel gas cannot meet the requirement of synthesis.

However, the elimination of tar and adjustment of H<sub>2</sub>/CO in fuel gas demands high reaction temperature since tar can cause some problems in the utilization of the product gas to the power generation and chemical conversion [4–6]. The most promising way is catalytic reforming of raw fuel gas.

Noble metal catalysts have excellent reforming activity and anti-coking performance. However, they are expensive and limited availability. Corella and co-workers investigated dolomite, CaO and MgO as active catalysts [3,7–11]. Another promising candidate of active components is Ni. Nickel based catalyst supported on the metal oxidation such as alumina is active and it is cheaper than other metal such as Pt and Rh [6,12–14]. Our group reported that NiO–MgO solid solution catalyst exhibited better performance in the reforming of biomass fuel gas conventional steam reforming

catalyst [4]. Development of Ni-based catalysts for steam reforming of biomass tar model compounds [15,16] and biomass powder [17] has been reported. The problem of Ni catalysts in the synthesis gas production process is coke deposition and it is necessary to develop the novel catalyst with high resistance to coke deposition. Honeycomb supporter can effectively reduce the carbon deposition on the catalyst surface because of special hole structure and the heat and mass transfer ability.

The goal of this work was to investigate the performance of steam reforming of biomass fuel gas over NiO–MgO solid solution cordierite monolith catalyst. Characterization and stability of the catalyst were also investigated.

### 1. Experiment

#### 1.1. Preparation of the catalysts

The nickel based cordierite monolith catalysts were prepared by wet impregnation of NiO and MgO on cordierite support whose surface area was increased by wet impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> superfine powder. The prepared method was described in detail as follows: The cordierite was first etched in 30 wt.% oxalic acid solution under vacuum for 30 min and then evaporated the water. After washed by distilled water, the support was dried overnight at 393 K. Then the surface area of the cordierite support was increased by wet impregnation with superfine  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder ethanolic solution. After dried overnight at 393 K, the support was calcined at 1023 K for 10 h. Repeating the process for three times,

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**Table 1**  
Physical characteristics and chemical composition of catalysts.

Parameter	Value		
Column height (mm)	50		
Outer diameter (mm)	40		
Cell density (cells cm <sup>-2</sup> )	60		
Wall thickness (mm)	1		
BET surface area of cordierite (m <sup>2</sup> g <sup>-1</sup> )	10.86		
BET surface area of catalyst (m <sup>2</sup> g <sup>-1</sup> )	40.2		
Component	Al <sub>2</sub> O <sub>3</sub>	MgO	NiO
Mass fraction (wt.%)	3.4	4.3	8.7

then the support was impregnated with nickel nitrate solution (72.38 g Ni(NO<sub>3</sub>)<sub>2</sub> and 200 ml distilled water) for 24 h. Then the catalyst was dried at 383 K overnight and calcined at 1073 K. Physical characteristic and chemical composition of the catalyst are listed in Table 1. The catalysts were prepared on supports of cordierite. The support had a honey-comb cross-section of a density of 60 cells/cm<sup>2</sup>. The catalysts were cylindrical in shape, with a height of 50 mm and a diameter of 40 mm.

### 1.2. Experiment

The scheme of experimental system used for steam reforming of biomass fuel gas is shown in Fig. 1. Experiments were carried out at atmospheric pressure in a fix bed quartz reactor (40 mm i.d.) places in a furnace. The monolith catalyst was held by ceramic support in the uniform temperature zone. The temperature was monitored by thermocouple near the monolith catalyst. The gap between the monolith catalyst and reactor wall was sealed with quartz fiber.

The composition of the biomass fuel gas was: H<sub>2</sub>: 16.04 vol.%, CO: 12.10 vol.%, C<sub>2</sub>H<sub>4</sub>: 2.50 vol.%, CO<sub>2</sub>: 21.95 vol.%, CH<sub>4</sub>: 15.08 vol.%, N<sub>2</sub>: 32.33 vol.%. The reforming reactor was atmospheric and temperature kept 1023 K. In order to investigate the tar cracking ability, tar from biomass gasification plant was added in biomass fuel gas. For all runs, the flow rate of biomass fuel gas

was 300 sccm. In the steam reforming runs, different steam/fuel (S/F) was added investigate the promotion effect of steam addition.

Firstly, the catalysts were reduced by mixed gas (H<sub>2</sub>/N<sub>2</sub> = 5/95, mol/mol) with flow rate of 300 sccm from room temperature to 1023 K within 2 h. Then reactant gases were feed into the reactor. After reforming runs was over, the pure N<sub>2</sub> was feed into reactor to cool the reactor 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.

### 1.3. Analysis

The contents of N<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub> 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 is TDX-01 and carrier gas is He. The contents of CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> were analyzed with another GC-9800 gas chromatograph equipped with a flame ionization detector. The column is Porapak Q and carrier gas is N<sub>2</sub>.

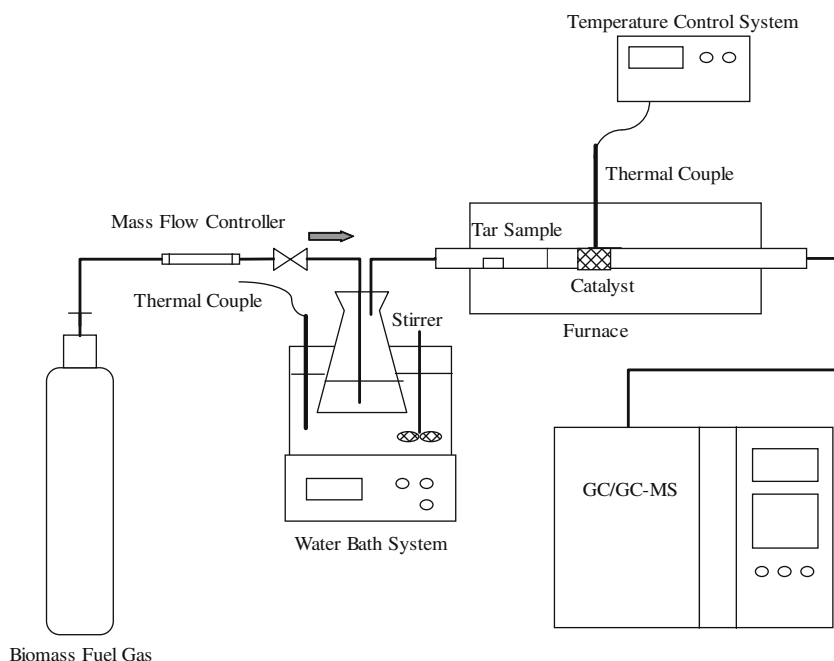
The products of tar cracking were analyzed by GC/MS (Agilent, Hp-1). The preconcentrator, GC and MS are Entech 7100, Agilent 6890, Agilent 6973 respectively.

### 1.4. Catalyst characterization

Biomass fuel gas was switched to N<sub>2</sub> after reforming at reaction temperature and kept for 10 min, the cooled to room temperature. Thermogravimetric analysis (TGAModal STA409PC, Germany), was used to measure the amount of carbon deposition on the catalyst surface. The temperature range was from 303 K to 1173 K with the raising rate of 10 K/min.

The major crystal phases of the catalyst samples were identified by X-ray diffraction using a BDX3300 diffractometer instrument with a Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm) at 40 kV and 30 mA. The Bragg angle step was 0.02°, and the scanning speed is 10 deg/min.

The morphology of the catalysts was analyzed by scanning electron microscopy using a JSM-6330F equipment, coupled with a



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

**Table 2**  
The results of steam reforming of biomass fuel gas.

S/F g/L	H <sub>2</sub> content (%)	CO content (%)	CH <sub>4</sub> content (%)	CO <sub>2</sub> content (%)	H <sub>2</sub> /CO	Con. CH <sub>4</sub> (%)	Con. CO <sub>2</sub> (%)
0.02	35.77	31.95	1.77	4.05	1.10	88.11	85.37
0.07	37.87	32.65	0.81	4.66	1.16	94.60	78.84
0.24	36.56	29.72	0.58	6.88	1.23	96.13	68.74
5.2	42.2	5.04	3.43	25.1	8.37	77.19	–14.1

Si/Li detector for energy dispersive spectrometer analysis, including point analysis and mapping of elements.

## 2. Result and discussion

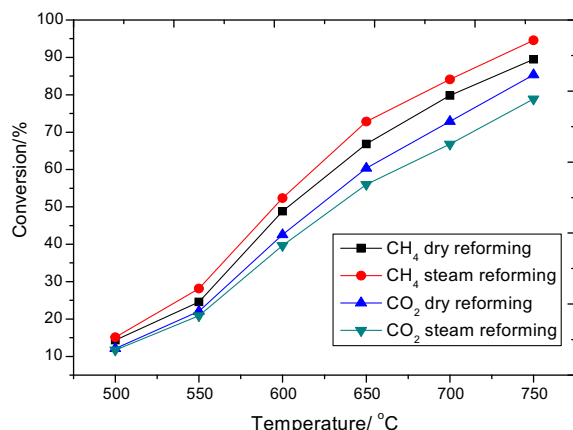
All experiments were at a constant molar flow rate of 300 mL per minute (sccm). The reactant S/F (g/L) gas ratio was defined as the steam addition per liter fuel gas. By this definition, experiments varied S/F ratio to investigate the performance of the steam reforming reaction. Tar captured in gasification plant was added in the fuel gas. The content of tar is 7.84 g/m<sup>3</sup>.

### 2.1. Performance of steam reforming

Reaction results at 750 °C for steam reforming of biomass fuel gas are shown in Table 2. The addition of steam can adjust the H<sub>2</sub>/CO in a wide range (from 1.1 to 8). The addition of steam also promoted CH<sub>4</sub> conversion, with the S/F ratio raised from 0.02 to 0.24, the conversion of CH<sub>4</sub> increased from 88.11% to 96.13%. More CH<sub>4</sub> conversion (CH<sub>4</sub> → C\* → CO\*) was caused by the OH\* provided by H<sub>2</sub>O. Vlachos and co-workers [18] reported that OH\* can convert CH<sub>4</sub> by pyrolysis and carbon oxidation. When S/F raised to 5.2 g/L, excessive steam in fuel gas reduce the temperature of the reaction system, so the conversion of CH<sub>4</sub> decreased to 77% which was caused by the decrease of reforming temperature.

The H<sub>2</sub> content in producer gas arranged from 35% to 42% and the CH<sub>4</sub> content decreased to 0.58% when S/F = 0.24 g/L. H<sub>2</sub>/CO ratio is 1.23, which indicated that the producer gas is suitable for synthesis of liquid fuel.

Fig. 2 shows that methane and CO<sub>2</sub> conversion over cordierite catalyst. It is particularly noted that there was a sharp rise with the temperature at around 550–650 °C which implies a high activation is required in both processes. Activation energy derived could be affected by the thermodynamic limitations. As a result, this value was derived from the temperature of below 550 °C where the conversions of methane and water were kept at below 35% (under a nearly plug flow reactor conditions). This result

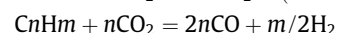
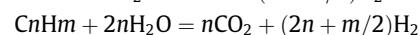
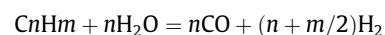


**Fig. 2.** Reaction temperature vs. gas conversion in different reforming ways.

matches with published using nickel catalysts [19]. Steam reforming shows higher CH<sub>4</sub> and CO<sub>2</sub> conversion than dry reforming.

H<sub>2</sub>/CO is very important for synthesis. As shown in Fig. 3, the H<sub>2</sub>/CO ratio after steam reforming is higher than that after dry reforming. It indicated that water gas shift reaction (WGSR) was carried out simultaneously in steam reforming process [20]. It is favorable at lower temperature and in the presence of steam, promoting H<sub>2</sub> production and consuming CO. So H<sub>2</sub>/CO ratio of synthesis gas increased.

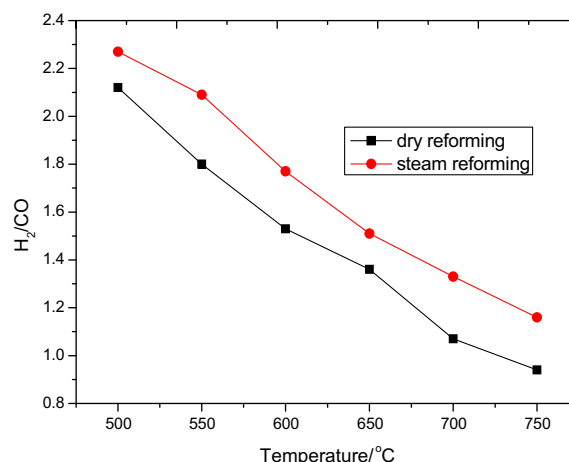
Because of the complexity of the gasification gas product, many parallel and consecutive reactions can take place during tar reforming.



Tar is a complex mixture of aromatics which includes a significant fraction of polycyclic aromatic hydrocarbons. Tar content varies from 5 to 75 g/m<sup>3</sup> in fluid bed gasifier. In this work, tar was collected from gasification plant. The tar content in biomass fuel gas was 7.86 g/m<sup>3</sup>. Table 3 shows the tar species analyzed by GC–MS. Tar species are mainly among C<sub>4</sub>–C<sub>10</sub>, familiar with the result from Milne and co-worker's results [21].

Lighter species (lower than C<sub>6</sub>) and naphthalene are completely converted in both dry reforming and steam reforming. Benzene and its derivants (C<sub>6</sub>–C<sub>9</sub>) still cannot completely converted. Benzene, derivants and the cracking product of naphthalene will have addition reaction with lighter hydrocarbons (as shown in Fig. 4). Some of the components are hard to convert in dry reforming, just like 2-methyl-phenol and methyl isobutyl ether, but the content of these organisms are tiny, so it will not be a very serious problem. But in steam reforming, all these organisms are completely converted to lighter hydrocarbons.

From Table 3 we find that steam reforming has better performance than dry reforming. The total tar conversion in steam reforming is higher than that in dry reforming. In both reforming

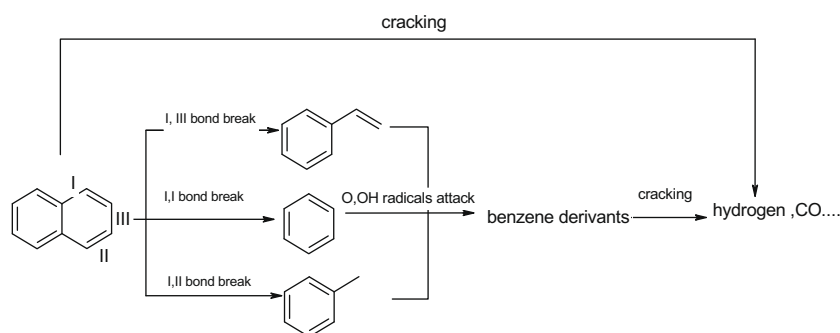


**Fig. 3.** Reaction temperature vs. H<sub>2</sub>/CO ratio in different reforming ways.

**Table 3**

The content of tar species in the inlet and outlet gas.

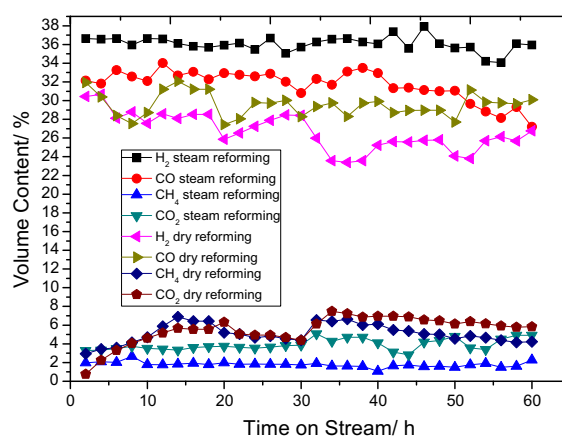
Species	Biomass fuel gas ( $\mu\text{g}/\text{m}^3$ )	Dry reforming ( $\mu\text{g}/\text{m}^3$ )	Conversion (%)	Steam reforming ( $\mu\text{g}/\text{m}^3$ )	Conversion (%)
<i>a</i> -Butene	138.282	1.030	99.25	0	100
Butane	7.789	0	100	0	100
Trans butane	61.800	0	100	0	100
Cis-butene	48.085	0	100	0	100
3-Methyl-1-butene	6.102	0	100	0	100
Pentylene	20.992	1.105	94.74	0	100
2-Methyl-1-butene	3.446	0	100	0	100
Isoprene	67.578	0	100	0	100
2-Methyl-2-butene	7.161	0	100	0	100
Cis-2-pentene	11.281	0	100	0	100
Cyclopentene	21.733	0	100	0	100
Benzene	3576.978	77.611	97.83	88.84	97.51
Toluene	1130.818	29.878	97.36	22.569	98.0
Ethylbenzene	112.241	3.331	97.04	5.668	94.95
<i>p</i> / <i>o</i> -Xylene	229.412	6.606	97.12	6.442	97.19
Styrene	1772.442	332.981	81.21	80.84	95.44
<i>m</i> -Xylene	65.220	3.841	94.11	5.094	92.19
2-Methyl-phenol	10.688	3.483	67.41	0	100
Phenol	0	1.922	Null	0	100
1,3-Cyclopentene	464.572	3.226	99.31	0	100
Methyl isobutyl ether	6.002	12.295	Null	0	100
Carbonyl Sulfide	26.232	0	100	0	100
Naphthalene	67.658	0	100	0	100
Total	7856.512	477.309	93.92	209.453	97.33

**Fig. 4.** Naphthalene conversion path.

methods, the tar content in synthesis gas reduced below  $0.5 \text{ mg}/\text{m}^3$ , the catalyst shows excellent tar elimination ability. For dry reforming,  $\text{CO}_2$  was considered as the only oxygen source, but in steam reforming  $\text{H}_2\text{O}$  can also be a very effective source. Efstathiou and co-worker found that in steam reforming process, H, O and OH radicals can all be found.

## 2.2. Catalyst stability

Steam reforming of biomass fuel gas is a very complex process, which include many reactions. Coke caused by tar,  $\text{CH}_4$  and CO can cover the surface of the catalyst, make the catalyst lose activity [22,23]. So life time runs was designed to test the stability of the catalyst in steam reforming conditions. Another 60 h runs of dry reforming was also carried out to make a comparison. As shown in Fig. 5  $\text{CH}_4$  and  $\text{CO}_2$  content decreased with the addition of steam. Steam in fuel gas can provide  $\text{OH}^*$  (main) and  $\text{O}^*$  as the oxidizer.  $\text{CH}_4$  and  $\text{CO}_2$  in fuel gas were consumed by the oxidizers [18]. The average content of  $\text{CH}_4$  and  $\text{CO}_2$  after steam reforming are 1.7% and 3%, which is much lower than that of dry reforming. The content of  $\text{H}_2$  and CO increased with the addition of steam. Especially the  $\text{H}_2$  content raised from 26% to 36%. It indicated steam reforming is suitable for  $\text{H}_2$  rich production and synthesis

**Fig. 5.** Syn-gas content vs. time on stream.

process. No  $\text{C}_2\text{H}_4$  molecular was detected which means  $\text{C}_2\text{H}_4$  in fuel gas was completely converted.

As shown in Fig. 6 with the reaction continues, the  $\text{H}_2/\text{CO}$  decrease in dry reforming, but keep constant in steam reforming.  $\text{CH}_4 = \text{C} + 2\text{H}_2$  and  $2\text{CO} = \text{C} + \text{CO}_2$  are thermodynamically feasible in dry reforming. As the formation of carbon assembled continuously

on the surface of the catalyst, more and more active points were covered. So the catalyst lose its activity. For steam reforming, carbon can react with steam to form CO and H<sub>2</sub>. So steam reduced the carbon deposition on the surface of catalyst. The catalyst keep the activity during the 60 h life time test. Average H<sub>2</sub>/CO in steam reforming reaches 1.12, higher than 0.9 in dry reforming. The addition of steam not only raised the H<sub>2</sub>/CO, but also promoted the stability of the catalyst.

### 2.3. Carbon deposition analysis

The catalytic reforming of CH<sub>4</sub>–CO<sub>2</sub> system has the problems of the deactivation by carbon deposition via Boudouard reaction ( $2\text{CO} = \text{CO}_2 + \text{C}$ ) and methane decomposition ( $\text{CH}_4 = \text{C} + 2\text{H}_2$ ) [24,25]. The deactivation via coke deposition may be more serious in the process of biomass fuel gas reforming because there is also some other light hydrocarbons and tar in the raw fuel gas. The coke can also formed remarkably by thermal and catalytic cracking and reforming of these hydrocarbons and tar [11]. The particulates and sulfur in the raw fuel gas stream are also responsible for catalyst deactivation [26].

After the long time experiments, we tested the carbon deposition via calculate the weight change before and after calcined the catalyst in air condition from room temperature to 800 °C. The results show that after 60 h dry reforming, there is 2.87 wt.% carbon deposited on the catalyst surface, but no weight change after steam reforming. Two samples of surface material on the surface of the catalyst were taken for TG test. As shown in Fig. 7, weight loss is much heavier in dry reforming catalyst than steam reforming catalyst. Results show that steam reforming can prevent the carbon deposition on the catalyst, as reported by Eftathiou [27].

This may because by several reasons.

- (1) Water in feed gas will react with CH<sub>4</sub> ( $\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$ ) and CO ( $\text{CO} + \text{H}_2\text{O} = \text{H}_2 + \text{CO}_2$ ) in the reforming process. It will effectively reduce the opportunities that Boudouard reaction and methane decomposition reaction happen.
- (2) Reaction between water and tar molecular will reduces the tar content and prevent the tar molecular adsorbed on the catalyst surface. This will prevent the carbon deposition on the catalyst.
- (3) Water in feed gas can dissociatively absorbed on the catalyst, hydroxylating the surface. At suitable temperature, the OH radicals can migrate to the metal sites, leading to oxidation of the intermediate hydrocarbon fragments and sur-

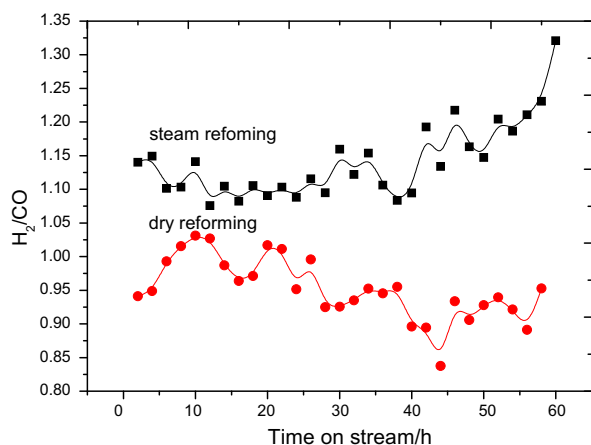


Fig. 6. H<sub>2</sub>/CO ratio vs. time on stream.

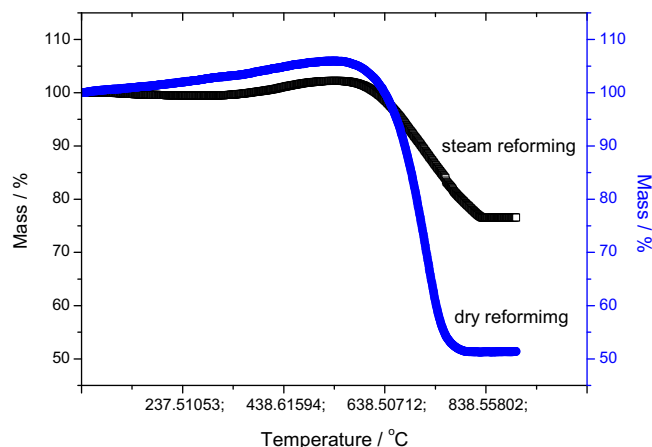


Fig. 7. TG curve after different reforming methods.

face carbon to CO + H<sub>2</sub>. MgO on the catalyst enables steam adsorption and increased surface carbon gasification rates [28].

- (4) The water addition provokes oxidation of the surface and improves the CO oxidation activity [29].

### 2.4. Characterization of catalysts

The XRD measurements for NiO–MgO cordierite catalysts are shown in Fig. 8. It was suggested that the fraction peaks at  $2\theta = 36.66^\circ, 65.22^\circ, 77.58^\circ$  could be assigned to nickel–magnesia solid solution and the peaks corresponding to Ni<sup>0</sup> was clearly observed for Ni/MgO catalyst [29]. The fraction peaks at  $2\theta = 44.42^\circ, 51.78^\circ, 76.3^\circ$  are assigned as Ni<sup>0</sup> and the fraction peaks at  $2\theta = 42.94^\circ, 62.18^\circ$  are assigned as NiO. The peak of Ni<sup>0</sup> was not observed over fresh catalyst. It may be due to the high dispersion of Ni particles on the catalyst surface. The XRD patterns of NiO–MgO are similar before and after reduction, which indicates that the bulk structure of the solid solution is maintained even after H<sub>2</sub> reduction and the nickel magnesite solid solution is formed, which makes the catalyst more stable.

The surface morphology of cordierite catalysts was shown in Fig. 9. The micrograph of the reduced catalyst revealed that the

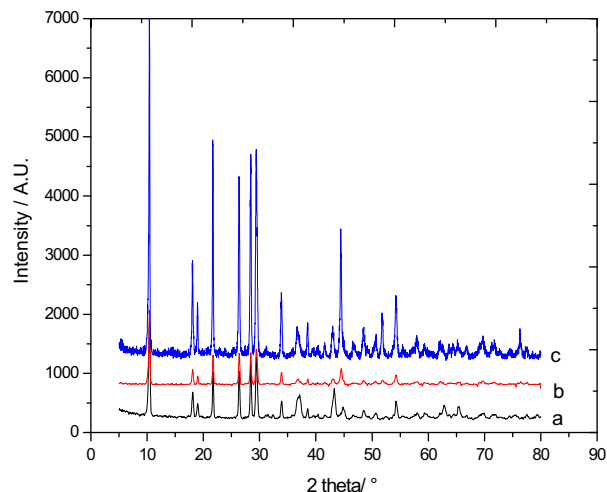


Fig. 8. XRD patterns of cordierite catalyst before and after reaction. (a) Before reduction. (b) After reduced. (c) Catalyst after 60 h steam reforming.



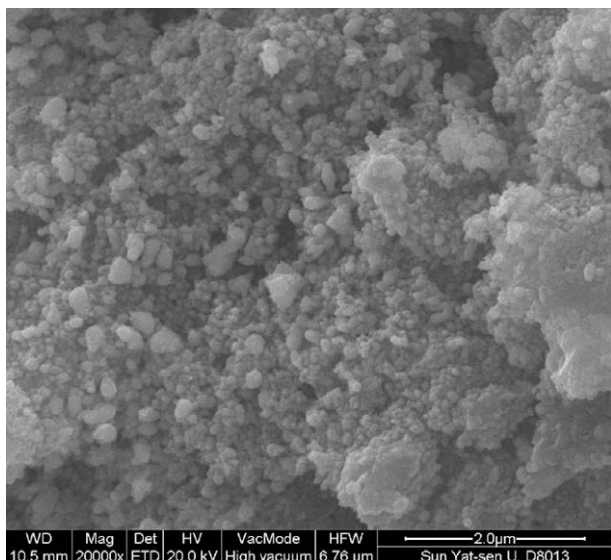


Fig. 9. SEM photo of the reduced catalyst.

samples were constituted of polydispersed spherical particles coexisted with amorphous mixed spheres which, according to the EDS probe, were probably  $\text{MgAl}_2\text{O}_4$  spinel structures. This is corresponding to the results reported in XRD (Fig. 8). The particle size of Ni measured by SEM photos tends to be larger than that obtained from XRD. This could be explained by the fact that the particles observed by SEM are hundred times as much as the coherent scattering area, the large particles consist of numerous small single crystal particles and they are agglomerates.

### 3. Conclusion

The NiO–MgO solid solution cordierite catalyst prepared by impregnation has an excellent stability and a highly activity for the dry and steam reforming of biomass fuel gas. Steam reforming process can effectively promote the  $\text{H}_2/\text{CO}$  ratio and tar conversion, which is attributed to the steam reforming reaction of methane and tar molecular. The addition of steam can also reduce the carbon deposition on the catalyst.

The result of characterization show that there are three main phases on the catalyst: NiO–MgO solid solution phase, NiO phase and Ni phase. High stability and activity for the reforming is attribute to nickel particles are highly dispersed on the catalyst.

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