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Steam reforming of biomass tar for hydrogen production over NiO/ceramic foam catalyst

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ABSTRACT

In this study, the catalytic steam reforming of biomass tar for hydrogen production was carried out in a fixed-bed reactor with NiO/ceramic foam catalyst. The ceramic foam used as catalyst carrier was a three-dimensional porous material with high porosity and high specific heat capacity. The effects of reaction temperature, steam to carbon ratio (S/C) and equivalence ratio (ER) on gas quality parameters were investigated. And the fresh, coked and regenerated NiO/ceramic foam catalysts were characterized by SEM and XRD analyses. It was found that, when the temperatures varied from 500 to 900 °C and S/C ratio from 0 to 4, H_2 yields were in the range of 28.29–105.28 g H_2/kg tar. With increasing ERs, the concentrations of H_2 decreased from 63.13 to 18.96%. SEM and XRD analyses showed that the catalyst was *in situ* activated by reducing nickel oxide to the active nickel metal during a reducing atmosphere in steam reforming process.
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Introduction

Biomass gasification is a promising thermo-chemical conversion technology for transforming biomass into renewable energy and value-added chemicals. However, a lot of biomass tar is produced in the process of gasification, which is the main barrier to realizing commercial-scale biomass gasification. The tar contains numerous organic compounds (acids, alcohols, aldehydes, ketones, etc), especially complex polycyclic aromatic compounds. Tar condensation can bring in operational burdens by blocking or corroding equipment such as gas cooler, filter and engine suction channels at a low temperature and by adding an increment in maintenance requirements [1,2]. In order to reduce the damage of tars, success in tars control and conversion is a severe issue for effective application of biomass gasification.

Considerable approaches including physical and thermo-chemical processes have been developed for tars elimination in recent years. The physical processes, such as scrubbers and filters have some limits. For example, scrubbing devices or filters are obliged to be frequently replaced for the reason of efficiency decrease [3,4]. Thermo-chemical process, such as thermal cracking, is one of the important methods for tar conversion, but the temperature is often operated over 900 °C. Thermal catalytic reforming could enhance the heating value of producer gas and the removal efficiency of tar, especially in terms of high hydrogen production spreads a desirable prospects [5]. Hydrogen is regarded as a clean and renewable energy for chemical applications, such as for the fuel cell with high efficiency and fuel combustion in motor vehicle or

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equipment. In particular, the only by-product of hydrogen combustion is water. So, hydrogen is considered as one of environment friendly fuel.

Tar steam reforming is a very attractive technique for tar removal, and catalytic steam reforming of tar for hydrogen production is one of promising routes, which had been reported extensively [6–9]. Several types of catalysts were employed in tar cracking, including natural minerals [10], alkaline earth metal catalysts [11], char [12,13] and Ni-based catalyst [14,15]. Ni-based catalyst often is considered as a steam reforming catalyst due to their high tar destruction activity. It is evident that the selection of support material is considered as one of the particularly crucial issues in tar steam reforming for hydrogen production [16]. Most commonly used supports are minerals and alumina or its modifier [17]. However, the mineral materials like dolomite, olivine owing to their low specific surface area and easy abrasion at higher temperatures [18], often lead to low hydrogen yield. In addition, alumina or its modifier cokes rapidly resulting in crippling catalytic activity in the tar reforming process. Ceramic foam is a three-dimensional porous material with high porosity and high specific heat capacity. It is widely applied in heat exchange materials, automobile exhaust device and heat recovery. According to the good physical properties of ceramic foam, it can be used as monolithic catalyst carrier for tar reforming, which might increase the rate of tar removal and hydrogen production. There are few reports on the ceramic foam which were used in tar reforming.

Most of hydrocarbons such as benzene, toluene, naphthalene, etc. were used as tar model compounds to simulate tar reforming. However, because the component of real tar is far complex than that of pure hydrocarbons, the behaviors of reforming are different from the former [19]. It is necessary to clarify the reaction mechanism of tar reforming for the potential practical application. Unfortunately, few literature focus on real tar reforming with monolithic catalyst for hydrogen production. In this study, the real tar from biomass gasification/pyrolysis process was chosen as feedstock for hydrogen production using the NiO/ceramic foam catalyst. A series of experiments are carried out to evaluate the influence of the reaction temperature, steam to carbon ratio (S/C) and equivalence ratio (ER) on gas products distribution and hydrogen yield. Meanwhile, the SEM and XRD analyses are used to characterize the properties of fresh, coked, regenerated NiO/ceramic foam catalyst.

Experimental section

Materials

The biomass tar for catalytic steam reforming was obtained from gasification of rice husk at 550 °C in a biomass gasification plant in Shandong province, China. The tar as a fluid, dark liquid with a strong pungent odour was firstly filtered to remove coke particles to avoid plugging the syringe pump. The ultimate analysis of biomass tar was measured on a CHN/O analyzer (Elementar, VarioEL, Germany). The lower heating value (LHV) was measured with oxygen bomb calorimeter. The ultimate analysis shows that the composition of biomass tar is 34.12% dry and ash-free basis (daf) carbon, 8.28% daf hydrogen, 2.00% daf nitrogen and 55.60% daf oxygen (calculated by difference to 100%). The LHV of tar sample is 13.43 MJ/kg. The density is 1.13 g/ml in 20 °C.

Catalyst preparation and characterization

The ceramic foam as carrier of catalyst is a cellular and lightweight structure consisting of solid ceramic material containing a high percentage of gas-filled pores. The Ni-based catalyst supported by ceramic foam was prepared by impregnation method. Typically, a certain amount of Ni $(NO_3)_2 \cdot 6H_2O$ was dissolved in deionized water to form a 1 mol/L of solution. Then, the ceramic foam (37 mm diameter, 50 mm long) was dipped into excess Ni $(NO_3)_2 \cdot 6H_2O$ solution for 2 h, and followed by drying at 105 °C for 12 h and calcining at 900 °C in muffle furnace for 2 h with a heating rate of 6 °C min^{-1}. The amount of NiO loading on the catalyst was controlled to be around 3.50%. The scanning electron microscopy (SEM) (Hitachi S-4800, Japan) with acceleration voltage of 15 kV and a resolution of 1 nm was used to observe the morphology of catalyst. The crystalline structures of the NiO/ceramic foam catalyst product were measured on EMPYREAN diffractometer (PANalytical, Holland) employing Cu Kα radiation at 40 kV and 40 mA. Diffraction patterns were recorded in the range of 2θ from 20° to 70° with a scanning step of 5°/min. The ceramic foam used in our study was produced with unified mould and raw material by a factory in China. In order to investigate the textural characteristic of ceramic foam support before and after impregnation, the specific surface area was determined by N_2 adsorption-desorption at −173 °C in a Quadrasorb-SI. The specific surface area of ceramic foam support and NiO/ceramic foam catalyst were 1.715 and 3.114 m^2/g, respectively. It is concluded from the result that the NiO particles loaded on the support surface increased the specific surface area of ceramic foam. The mineralogical analyses show that the chemical compositions of ceramic foam are 79.24% Al_2O_3, 19.29% P_2O_5, 0.77% SiO_2, 0.16% Na_2O, 0.10% Fe_2O_3 and other metal oxides (including ZrO_2, CaO, TiO_2, K_2O and ZnO) less than 0.10%.

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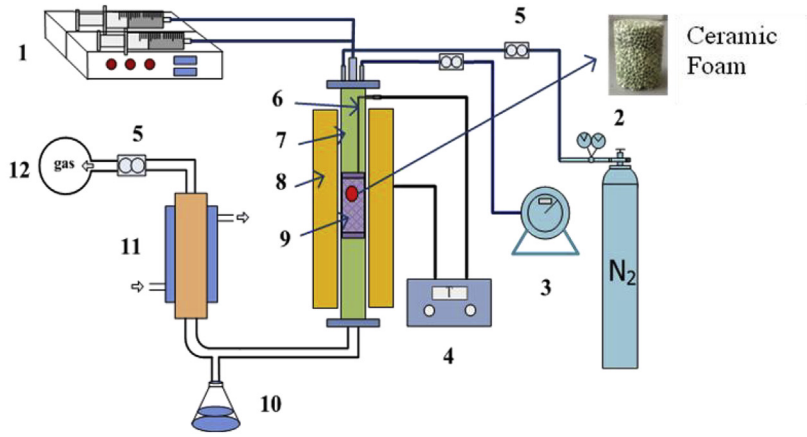
Apparatus and catalytic tests

The experimental apparatus used for a lab-scale catalytic steam reforming is depicted in Fig. 1. Experiments were carried out under atmospheric pressure in a tubular fixed-bed reactor, which was heated externally by electrical furnaces (1.5 kW, 220 V) with a stainless steel tube (40 mm diameter, 500 mm long). The ceramic foam loaded nickel oxide was carefully placed in the middle of reactor to get uniform temperature. The reaction temperature was monitored by a K-type thermocouple placed inside the tube near catalyst. Tar and water were evaporated at 105 °C, and were fed by a double channel micro-infusion pump (Smith Medical, China) into furnace. N_2 was used as carrier gas regulated by mass flow



1. Double channel micro-infusion pump; 2. Nitrogen cylinder; 3. Air pump; 4. Temperature controller; 5. Mass flow meter; 6. K-type thermocouple; 7. Fixed-bed reactor; 8. Electrical furnaces; 9. NiO/ceramic foam catalyst; 10. Liquid collector; 11. Condenser; 12. Tedlar gas bag.

Fig. 1 – Schematic of the tar steam reforming apparatus.

meter. Air was supplied by an air pump. A condensation unit was applied for separation of the synthetic gas and liquid. The volume of non-condensable gas was measured by a flow-meter after a condensation unit. The product gases collected in Tedlar gas bag were analyzed off-line by Techcomp GC7890II gas chromatography with thermal conductivity detector (TCD) for determining H_2, O_2, N_2, CO and CO_2 analyses, and with a flame ionization detector (FID) for CH_4, C_2H_4, C_2H_6, C_3H_6 and C_3H_8 analyses. It should be pointed out that all experiments were carried out about 2 h mainly caused by large weight hourly space velocity (WHSV). In our work, each test reached a stable state in half an hour. The gas samples were collected by gas-bag every 20 min. The catalytic activity of the NiO/ceramic foam, product composition, lower heating value (LHV), gas density, H_2 yield and H_2 selectivity were determined and calculated with formulas (1)–(6).

$$\text{Gas concentration (\%)} = \text{mole of single gas product/(total moles of gas products)*100\%} \quad (1)$$

$$\text{LHV of dry product gas (MJ/Nm}^3\text{): LHV} = 10.83H_2 + 12.61CO + 36.02CH_4 + 64.55C_2H_4 + 93.39C_2H_6 + 59.62C_3H_6 + 87.76C_3H_8 \quad (2)$$

$$\text{Gas density (kg/Nm}^3) = 0.09H_2 + 1.25CO + 1.98CO_2 + 0.72CH_4 + 1.25C_2H_4 + 1.36C_2H_6 + 1.88C_3H_6 + 1.97C_3H_8 \quad (3)$$

where H_2, CO, CH_4, C_2H_4, C_2H_6, C_3H_6 and C_3H_8 are the molar percentages of product gas.

$$H_2 \text{ yield (g } H_2\text{/kg tar)} = \text{mass of } H_2 \text{ produced/mass of tar} \quad (4)$$

$$H_2 \text{ selectivity (\%)} = \text{moles of } H_2 \text{ produced /moles of C atoms in gas phase /2.235*100\%} \quad (5)$$

where 2.235 is the H_2/CO_2 ration, which depends on gas products from complete tar reforming. Tar corresponds to the average composition $CH_{2.91}O_{1.22}$ by the ultimate analysis.

Tar complete reforming:

$$CH_{2.91}O_{1.22} + 0.78H_2O = CO_2 + 2.235H_2 \quad (6)$$

Results and discussion

The effect of reaction temperature

The reaction temperature has a profound influence on tar reforming with NiO/ceramic foam catalyst. The reaction temperature was in a range of 500–900 °C at an increment of 100 °C. The operating conditions and test results are summarized in Table 1 and Fig. 2. Fig. 2 showed that the major components of producer gas from tar reforming were H_2, CO, CO_2, CH_4, and other small molecular organic gases, such as C_2H_4, C_2H_6, C_3H_6 and C_3H_8. H_2 concentration first increased from 50.04 to 64.92 % in the temperature of 500–600 °C, and then a slight decrease from 64.92 to 57.97 % was observed between 600 and 900 °C. It is noted that the CO concentration increased from 2.67 to 25.61 % as the reaction temperatures increased, while CO_2 concentration varied from 44.45 to 14.37 % oppositely. The contents of alkane were low in comparison with other inorganic molecules. The content of CH_4 was below 3%, and the C_2–C_3 gaseous almost remained below 0.05% under different reaction temperatures. The results indicated that the hydrocarbons were likely formed by cracking of oxygenated organic compounds and then easily catalyzed by NiO/ceramic foam catalyst. As for the gas density and LHV of gas produced from tar reforming, the gas density presented a declining trend. On the contrary, the lower heating value showed a sharp rise as the reaction temperatures increased from 6.79 MJ/Nm^3 to 10.26 MJ/Nm^3 between 500 and 900 °C. It

Table 1 – The experimental results of reaction temperature. (The tar feed rate (g/h) is 6.78; ER is zero; the amount of catalyst loading is 3.54%; the ratio of S/C and weight hourly space velocity (WHSV) (h^{-1}) is controlled at 1 and 4.68, respectively.)

Reaction temperature (°C)	Gas density (kg/Nm^3)	Gas yield (m^3/kg tar)	Lower heating value (MJ/Nm^3)	Hydrogen yield (g H_2/kg tar)	H_2/CO	H_2 selectivity (%)
500	0.98	1.45	6.79	64.74	18.75	44.81
600	0.73	1.53	7.41	88.63	30.13	82.81
700	0.69	1.87	8.49	105.28	5.12	76.59
800	0.69	1.77	9.32	94.77	2.88	66.9
900	0.67	1.66	10.26	85.74	2.26	61.64

is observed (from Table 1) that gas and hydrogen yields increased, reaching the maximum at 700 °C and then dropped. This trend can be explained by that higher temperature favors endothermic reactions. The mechanism of catalytic tar reforming can be described by the following reactions shown in Eqs. (7)–(10):

$$\text{Tar reforming: Tar} + H_2O \rightarrow H_2 + CO + CO_2 + CH_4 + \text{hydrocarbons} + \ldots \ \Delta H > 0 \quad (7)$$

$$\text{Hydrocarbons reforming: Hydrocarbons} + H_2O \rightarrow H_2 + CO + CO_2 \ \Delta H > 0 \quad (8)$$

$$\text{Water-gas shift reaction (WGSR): } CO + H_2O = CO_2 + H_2 - 41 \text{ kJ/mol} \quad (9)$$

$$\text{Boudouard: } CO_2 + C = 2CO + 172 \text{ kJ/mol} \quad (10)$$

The evolution of gas concentration and yields are first attributed to fast pyrolysis of tar at the beginning of reforming. And then, the evolved gases are reformed with the ceramic foam catalyst based on the reactions mentioned above (Eqs. (7)–(10)). Actually, the reforming process occurred in a reducing atmosphere, and the catalyst of NiO was reduced to nickel metal in a short time, which is the main active ingredient in the reforming reaction. Because higher temperature is in favor of endothermic reactions, the increase in temperature has a great influence on the production of H_2, CO and CO_2, and the cracking of tars is strengthened. In addition, the ceramic foam used as catalyst carrier has large capacity of heat, and it can keep the temperature of reaction field in a stable condition. Therefore, the negative effects caused by reaction temperature fluctuating might be reduced. The hydrogen yield reached a maximum value of 105.28 g H_2/kg tar at 700 °C, and beyond this temperature, the hydrogen yields declined slightly. It suggested that with the increase of temperature, tars are more easily to be decomposed into small molecules such as H_2, CO. These results are in agreement with Świerczyński et al. [20] who had reported that the concentrations of H_2, CO and CO_2 were related to the temperature dependence of the water-gas shift reaction (Eq. (9)).

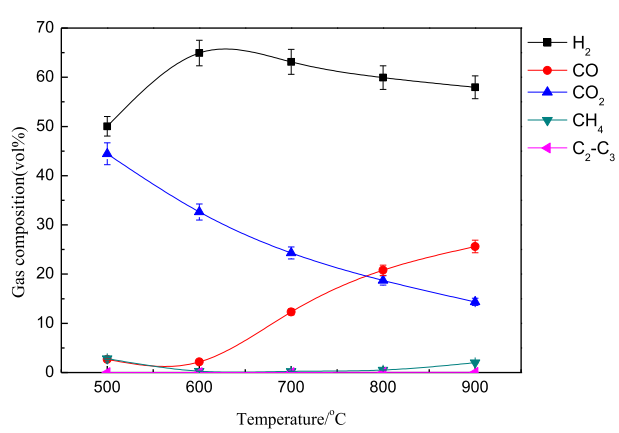


Fig. 2 – The effect of reaction temperature on gas composition.

For the WGSR, high temperature is adverse for hydrogen production because of its exothermic nature. As temperature increases, the tendency shifted towards reactants due to Le Chatelier's principle [21]. This might be the reason that the gas and hydrogen yields decrease at temperatures higher than 700 °C. The H_2 yield is significantly higher than many other studies that had been reported. Davidian et al. [22] and Iojoiu et al. [23] had produced 30–40 g of hydrogen per kilogram of fast pyrolysis bio-oil by catalytic cracking on nickel and noble metal catalysts. To enhance the efficiency of H_2 yield, a balance of temperature should be established between the energy consumption and tar conversion. The catalytic steam reforming could be carried out at a lower temperature than that used in non-catalytic steam reforming [24]. The favorable reaction temperatures observed in catalytic steam reforming were between 650 and 750 °C. In addition, as the ceramic foam used for catalyst carrier is rich in pores, the tars might be more likely to be captured and catalytically cracked into small molecule gases such as H_2, CO, CO_2 and C_2–C_3.

The increased temperature also had an effect on H_2/CO and H_2 selectivity. As the H_2/CO ratios are between 1 and 2 ($1 < H_2/CO < 2$), the syngas ($H_2 + CO$) could be applied to produce chemical products such as methanol, pure naphtha [25,26]. From Table 1, It can be observed that the H_2/CO ratio and H_2 selectivity firstly increased from 500 to 600 °C sharply, and then decreased with further increasing temperature (>700 °C). These results suggested that reforming reaction was thermodynamically favorable with catalyst at lower temperature. And the sudden rise in CO production at the higher temperatures (>700 °C) may also contribute to the boudouard reaction mentioned in Eq. (10). The variation of high H_2 selectivity from 44.81 to 82.81% demonstrated a large potential of catalytic steam reforming of tar for hydrogen production. The maximum H_2/CO ratio and H_2 selectivity were 30.13 and 82.81% at 600 °C, respectively.

The effect of steam to carbon ratio (S/C)

The steam to carbon ratio plays an important role in reforming of tars, which varies from 0 to 4 at 700 °C in this study. The feed rates of tar and steam were controlled with a two-channel trace injection pump. The feeding rate of tar was kept constant and the feed rate of steam was varied to adjust S/C ratios. The operation conditions and experimental results are summarized in Table 2.

The effect of S/C ratio on gas component is shown in Fig. 3. It can be found that the variation of gas contents showed monotonous trend while the increase of S/C ratio from 0 to 4. In the S/C range of 0–2, the concentrations of H_2 and CO_2 increased obviously from 41.75 to 63.13% and from 15.19 to 31.67%, respectively. The maximum H_2 concentration reached 63.13% at S/C = 1, and the maximum CO_2 reached 31.67% at S/C = 2. The concentrations of CO, CH_4 and C_2–C_3 presented reverse trends, which decreased from 27.36 to 7.31%, 12.37 to 0.39% and 2.86 to 0.02% with increasing ratios of S/C, respectively. However, the gas content almost had no significant difference at higher S/C ratios (S/C > 2). Hydrogen yield (see in Table 2) reached maximum value of 105.28 g H_2 per kg tar at S/C = 1, then declined in the S/C ratio range of 1–4. The lower heating value continuously declined.

This is because the increased steam supply favors the equilibrium of tar reforming reaction (Eqs. (7)–(8)) and the water-gas shift reaction (Eq. (9)). As a result, it is shown that the concentration of hydrogen increased and carbon monoxide decreased in the range of S/C ratio from 0 to 2. As the ratio of S/C greater than 2, a slight change of gas concentration may be due to adsorption saturation of steam on catalyst surface [20], which caused the activity of catalyst decease. Unfavorable reactions responsible for carbon formation have to be considered by decomposition of hydrocarbon gas and CO disproportionation (Eq. (10)). Two approaches are employed to prevent carbon depositing. The first one is to enhance steam adsorption with carbon or carbon precursors on the catalyst surface. The second one is to modify the catalyst via adding other metal additives [27,28].

Actually, two problems are often confronted in real reforming reaction, on the one hand, insufficient steam may result in the low H_2 yield as well as low H_2 concentration due to incomplete reactions during the tar reforming. As a result, the reforming reactions (Eqs. (7)–(8)) and water gas shift reaction (Eq. (9)) can not achieve the state of completion. On the other hand, in addition, at a high S/C ratio, sufficient steam is used to drive tar cracking and reforming which leads to higher gas and hydrogen yields. Furthermore, higher water partial pressure favors the equilibrium of water gas shift reaction (Eq. (9)) toward hydrogen formation and can reduce coke deposition on the catalyst by promoting the gasificaton of carbonous intermediates. Nevertheless, excessive steam may lead to some adverse effects. The first one is excessive water may cause additional energy consumption in separation steam from dryness of produced gas as well as in the condensation process. The second one is the decrease of tar decomposition caused by the decrease of reforming temperature due to plenty of heat were absorbed by steam. This result was verified by Tao et al. [29] who used toluene as tar model on Ni-based catalyst. And they found with increasing the S/C ratios from 2 to 5, the toluene conversions were firstly increased then decreased, and the maximum conversion was obtained at S/C ratio of 3. So an optimal S/C ratio may exist in different operating conditions. In our work, S/C = 1 was found to be the optimal ratio under the examined operating condition (Table 2). It can be also seen from Table 2 that H_2/CO ratios increased sharply from 1.53 to 9.52 as the S/C ratios increased from 0 to 3, while decreased slightly at S/C of 4. And the H_2 selectivity varied from 30.81 to 68.83 %.

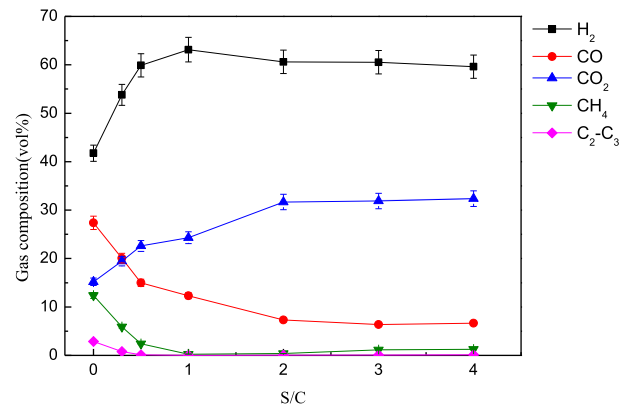


Fig. 3 – The effect of S/C ratio on gas composition.

The effect of equivalence ratio (ER)

The equivalence ratio (ER) is defined as the ratio of the actual air supplied into the reformer relative to the stoichiometric air required for complete combustion of tar, which also is an

Table 2 – The experimental results of different S/C ratio. (Reaction temperature is 700 °C; ER is zero; the amount of catalyst loading is 3.54%; the tar feed rate (g/h) is 6.78 and the weight hourly space velocity (WHSV) (h^{-1}) is controlled at 4.68.)

S/C	Gas density (kg/Nm^3)	Gas yield (m^3/kg tar)	Lower heating value (MJ/Nm^3)	Hydrogen yield (g H_2/kg tar)	H_2/CO	H_2 selectivity (%)
0	0.81	0.76	14.43	28.29	1.53	30.81
0.3	0.74	1.16	11.04	55.53	2.68	51.12
0.5	0.71	1.21	9.32	64.92	4.00	66.64
1	0.69	1.87	8.49	105.28	5.12	76.59
2	0.78	1.57	7.64	85.11	8.29	68.83
3	0.77	1.08	7.83	58.11	9.52	68.47
4	0.79	0.84	7.83	44.81	8.97	65.85

important parameter in the tar reforming process. The ERs were varied from 0 to 0.4 in this study. The experimental conditions and results are presented in Table 3 and Fig. 4. With increasing ERs, the concentrations of H_2 decreased from 63.13 to 18.96% gradually, and the CO_2 concentrations increased from 24.29 to 55.81%. CO contents showed fluctuant variation in the range of 12.32–23.72%. Furthermore, the fractions of CH_4 and C_2–C_3 remained at low level in the whole range of ER, and the maximum molar fractions of CH_4 and C_2–C_3 were 5.14% and 2.02%, respectively. Accordingly, the ratios of H_2/CO changed from 5.12 to 1.02, while the H_2 selectivity decreased linearly from 76.59 to 10.26%.

The ER influences on produced gas may be explained by the following reasons. First, a large amount of air is fed with the increase of ER, as a result, more N_2 is brought into the reactor. Although nitrogen do not participate in any reaction, part of heat will be taken away by N_2 flow leading to the decreased temperature of ceramic foam, which is adverse for the tar reforming occurring inside of ceramic foam. Second, a high value of ER represents that more H_2 and CO was burn with O_2 into H_2O and CO_2. On the one hand, high ER causes the concentration of combustible gas (H_2, CO) loss, which decrease hydrogen yield. Consequently, gas yields first increased (after gas condensation) from 1.87 to 1.90 m^3/kg tar, then declined from 1.90 to 0.47 m^3/kg tar and hydrogen yield decreased from 105.28 to 7.97 g H_2/kg tar with the increase of ER. On the other hand, an increase in ER will raise the temperature of reformer, which can keep the furnace temperature in a suitable level. Guo et al. [30] and Lv et al. [31] investigated that the pyrolysis zone temperature was relatively lower than the combustion zone where oxidation reactions release large heat to reach the peak temperature. From Fig. 4, while excessive air led to large H_2 and CO consumption, more CO_2 and H_2O were generated and as a result, the quality of product gas deteriorated and the lower heating values decreased. So, a balance of quality of production, heat loss and generation of reaction should be considered as the ER increases. In addition, as ER increases, more air was introduced into the reactor, the carbon deposited on the ceramic foam catalyst surface might be oxidized, and as a result, the life of catalyst extended. Some new methods of the removal of carbon deposition on the ceramic foam catalyst are testing in our group, which will be reported in the near future.

SEM analysis

The scanning electron microscopy (SEM) was applied to observe the morphology of the fresh, coked and regenerated catalysts after reaction at 700 °C, S/C of 1, ER of 0 and WHSV of 4.68. The images of all catalysts are shown in Fig. 5.

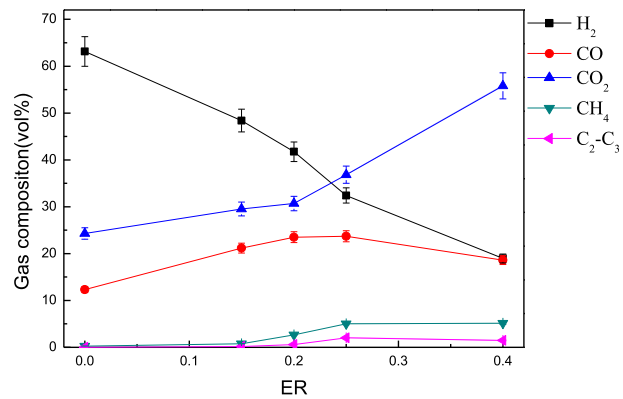


Fig. 4 – The effect of equivalence ratio on gas composition.

For fresh catalyst shown in Fig. 5 (a), the NiO crystals cover on the surface of three-dimensional ceramic foam. Fig. 5 (b) shows the morphology for coked catalyst. After reforming of tar, a non-structure coke closely relating to the nature of aromatic compound was observed with few metal particles on the surface. It is generally known that the accumulation of carbon can prevent the catalyst site from contacting with steam. Besides, the blockage of carbon deposition is usually considered as the primary reason for catalyst deactivation. So, it is necessary to regenerate the catalyst to remove the carbon deposition after reaction for a period of time. In this work, the coked catalyst was *in situ* regenerated by introducing a large amount of air into the reactor at 700 °C for 10 min to oxidize the deposited carbon on the surface of catalyst. After regeneration, as show in Fig. 5 (c), an aggregation of spherical homogeneous grains was also observed, which are mainly NiO grains identified by X-ray diffraction (XRD) analysis.

XRD analysis

In order to investigate the association of catalyst phase changes, the crystalline structures of the fresh, coked, regenerated catalyst characterized by XRD after reaction at 700 °C, S/C of 1, ER of 0 and WHSV of 4.68 are presented in Fig. 6. All catalysts showed characteristic diffraction peaks corresponding to α-Al_2O_3 ($2\theta = 25.6$, 35.2, 37.8, 43.4, 52.6, 57.6, 66.6 and 68.3°) and an obvious line corresponding to SiO_2 ($2\theta = 21.6°$), which are in good agreement with the XRF of ceramic foam.

Table 3 – The experimental results of equivalence ratio. (Reaction temperature is 700 °C; S/C is 1; the tar feed rate (g/h) is 6.78; the amount of catalyst loading is 3.40% and the weight hourly space velocity (WHSV) (h^{-1}) is controlled at 4.11.)

Equivalence ratio	Gas density (kg/Nm^3)	Gas yield (m^3/kg tar)	Lower heating value (MJ/Nm^3)	Hydrogen yield (g H_2/kg tar)	H_2/CO	H_2 selectivity (%)
0	0.69	1.87	8.49	105.28	5.12	76.59
0.15	0.90	1.90	8.30	82.16	2.29	41.80
0.20	0.99	1.42	7.94	56.62	2.67	35.50
0.25	1.12	1.28	7.93	38.80	3.01	25.91
0.40	1.41	0.47	7.25	7.97	1.02	10.26

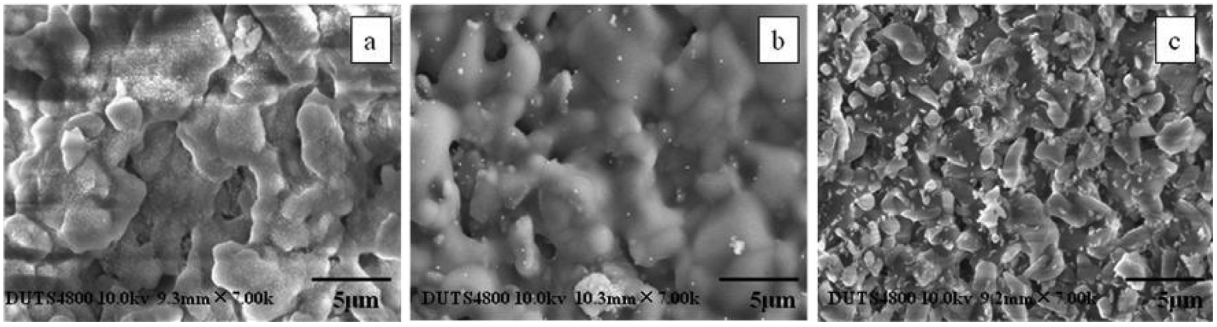


Fig. 5 – SEM of images of NiO/ceramic foam catalyst for steam reforming of tar (a) fresh catalyst (b) coked catalyst (c) regenerated catalyst.

The fresh NiO/ceramic foam XRD pattern showed broad lines corresponding to NiO (2θ = 37.3,43.3 and 62.9°), indicating the presence of large size aggregates and the availability of catalytic sites after activation, however, no lines matching pure Ni phases were identified. After reforming, similar trends can be also observed for coked catalyst. The main lines of nature ceramic foam close to α-alumina were observed suggesting that the support structure remains unchanged. No strong diffraction peaks corresponding to NiO was visible while two main strong lines attributing to metallic Ni (2θ = 44.5and 51.9°) appeared. This implied that the catalyst was *in situ* activated by reducing nickel oxide to nickel metal, which was considered as the main active phase at reducing atmosphere in steam reforming process. After regeneration, the diffraction peaks of metallic Ni disappear along with lines corresponding to NiO being observed again. It signifies that the active component of catalyst can be recovered by regular regeneration via carbon deposition combustion. The catalytic activity after regeneration will be reported later.

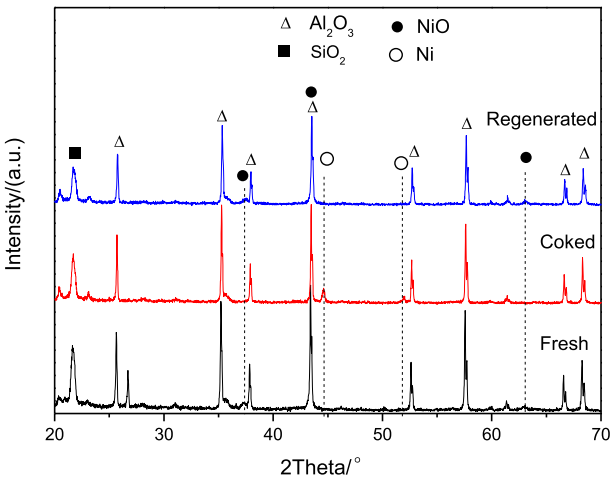


Fig. 6 – XRD patterns of catalyst in fresh, coked and regenerated states.

Conclusion

In present work, steam reforming of tar using NiO/ceramic foam catalyst for hydrogen production prepared was investigated. It was found that the hydrogen yield of tar reforming reached up to 105.28 g H_2/kg tar at 700 °C. In the S/C range of 0–4, the H_2 concentrations increased from 41.75 to 63.13%. However, the increased of ER values from 0 to 0.4 reduced H_2 yields sharply from 105.28 to 7.97 g H_2 per kg tar. SEM was used to observe the morphology of the fresh, coked and regenerated catalysts. XRD analyses showed that the catalyst was *in situ* activated by reducing nickel oxide to active nickel metal at reducing atmosphere.

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