

Experiments on Ni/ γ -Al₂O₃ catalyst for improving lower heating value of biomass gasification fuel gas via methanation

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Abstract: Ni-based catalysts supported by γ -Al₂O₃ were prepared for improving the lower heating value (LHV) of biomass gasification fuel gas through methanation. Prior to the performance tests, the physico-chemical properties of the catalyst samples were characterized by N₂ isothermal adsorption/desorption, X-ray diffraction (XRD) and a scanning electron microscope (SEM). Afterwards, a series of experiments were carried out to investigate the catalytic performance and the results show that catalysts with 15% and 20% Ni loadings have better methanation catalytic effect than those with 5% and 10% Ni loadings in terms of elevating the LHV of biomass gasification fuel gas. Moreover, controllable influential factors such as the reaction temperature, the H₂/CO ratio and the water content occupy an important position in the methanation of biomass gasification fuel gas. 15Ni/ γ -Al₂O₃ and 20Ni/ γ -Al₂O₃ catalysts have a higher CO conversion and CH₄ selectivity at 350 °C and the LHV of biomass gasification fuel gas can be largely increased by 34.3 % at 350 °C. Higher H₂/CO ratio and a lower water content are more beneficial for improving the LHV of biomass gasification fuel gas when considering the combination of both CO conversion and CH₄ selectivity. This is due to the fact that a higher H₂/CO ratio and lower water content can increase the extent of the methanation reaction.

Key words: Ni-based catalyst; methanation; biomass gasification fuel gas; lower heating value

DOI: 10.3969/j.issn.1003-7985.2017.04.010

It is generally accepted that energy and fossil fuel consumption are crucial to industrial and economic development. However, traditional fossil fuels such as coal and petroleum have a limited storage amount and also can cause various severe environmental problems such as air pollution and the greenhouse effect during use. Biomass fuel gas generated from gasification of organic materials rooting in forestry and agricultural residues, for instance, wood and straw, can be utilized as an alternative, clean

and supplementary source of fuel^[1]. Hence, production of biomass fuel gas through gasification has attracted more and more attention recently due to the increasing market demand and the encouragement of the national energy policy. Nevertheless, the lower heating value (LHV) of some types of biomass gasification fuel gas is relatively small (2 to 6 MJ/m³ under standard temperature and pressure) due to different biomass sources and gasification conditions^[2-6]. From perspective of combustion, a smaller LHV potentially implies a larger amount of fuel gas when the same amount of heat is in need, which accordingly raises the operation costs of a few factories and plants. Furthermore, gas appliances are designed in accordance with certain heating values. Biomass gasification fuel gas with an insufficient heating value might cause undesired damage to them and influence the efficiency of combustion. Therefore, it is economically and securely meaningful to improve the LHV of biomass gasification fuel gas.

Two technologies have been frequently employed to enhance the lower heating value of biomass gasification fuel gas: 1) Decreasing the content of N₂ contained in the gas; 2) Converting CO and H₂ into CH₄ through methanation. The first technology normally includes the process of N₂ separation from the product gas, which correspondingly increases the content of toxic CO and explosive H₂, thus increasing the complexity and risk to the system. Besides, choosing some novel substances such as steam^[7-8] or oxygen-enriched air^[9-10] as biomass gasification agents can reduce the dilution effect of N₂ on the LHV of biomass gasification fuel gas as well. Similarly, this method may also decrease maneuverability. Methanation of syngas has been investigated extensively over a century. It is generally applied to produce high purity methane from syngas (CO + H₂) out of coal gasification or to remove CO from ammonia synthesis feed gas (N₂ + H₂) in ammonia plants^[11-12]. In recent years, this technology has played a significant role in the elimination of CO impurities from reformat gas for polymer electrolyte fuel cells (PEFCs) or polymer electrolyte membrane fuel cells (PEMFCs)^[13-14]. However, from the current literature, applying the technical approach of methanation into the biomass gasification fuel gas system for LHV enhancement is rarely reported.

According to the research results of Ma et al.^[15], the CO disproportionation reaction, also known as Boudouard

Received 2017-05-19, **Revised** 2017-09-04.

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Foundation item: The International S&T Cooperation Program of China (No. 2014DFE70150).

Citation: Dong Xinxin, Jin Baosheng, Wang Yanyan, et al. Experiments on Ni/ γ -Al₂O₃ catalyst for improving lower heating value of biomass gasification fuel gas via methanation[J]. Journal of Southeast University (English Edition), 2017, 33 (4): 448 – 456. DOI: 10.3969/j.issn.1003-7985.2017.04.010.

reaction^[16] which leads to carbon deposition, can be inhibited by adding water vapor to the system. Considering the existence of water during our research, the effect of this side reaction can be ignored. The main reaction in our system, which refers to methanation reaction, is highly exothermic. Massive chemical energy will be transformed into thermal energy with the reaction proceeding, which naturally causes a considerable loss of energy, thus leading to the reduction of thermal efficiency. In addition, the volumetric flow rate of the product gas will decrease with the increase in the generation of CH₄ since the methanation reaction belongs to volume-reduced reactions. Inadequate product gas volume will have impact on the use continuity of gas appliances. Consequently, sufficient assurance of product gas volume should be taken into consideration for the purpose of industrial application when aiming at increasing the LHV of the biomass gasification fuel gas through methanation. Though the LHV of pure CH₄ is higher than that of single-component CO and H₂ (35.914, 12.636 and 10.785 MJ/m³ for CH₄, CO and H₂, respectively), the formation of CH₄ is based on the CO and H₂, which also have a certain amount of heating value that can partially account for the total LHV of the biomass gasification fuel gas. In a nutshell, it is not optimum to carry out methanation as thoroughly as possible from those aspects above.

The key factor of methanation is the catalyst and vast quantities of noble-metal and transition-metal methanation catalysts have been studied^[17]. In comparison with metals such as Ru, Rh and Co^[18–20], the Ni-based catalyst is more appealing for methanation due to its massively successful industrial application and lower market price. Many efforts have been made to enhance the performance of the Ni-based methanation catalysts in order to produce a higher quality methane or to remove CO from the ammonia synthesis feed gas more thoroughly. The results of Lu et al.^[21] indicated that VO_x can promote the dissociation of CO in the methanation reaction and thus yield more methane. Kim et al.^[13] reported that Ir-doped Ni catalysts showed the best performance for decreasing the CO content from reformat gas below 10×10^{-6} at 190 to 230 °C. As for the catalyst support, various metal oxides such as Al₂O₃, SiO₂, ZrO₂ and TiO₂ can be used as methanation catalyst support. Of all these materials, Al₂O₃ is the most typical one for methanation. Liu et al.^[22] systematically compared three Ni-based catalysts and concluded that the low-temperature activity of the three catalysts are in the order of Ni/Al₂O₃ > Ni/ZrO₂ > Ni/CeO₂. Unlike the systems mentioned above, our goal in this work is to improve the heating value of biomass gasification fuel gas by partial methanation. As a result, there is no need to remove CO as utterly as possible by selective methanation or to produce high quality methane by complete methanation on the premise of the expected

requirements. Accordingly, the catalysts employed in the biomass gasification fuel gas system will act differently from those catalysts described above.

In this paper, with the purpose of studying the feasibility and practicality of biomass gasification fuel gas LHV improvement through methanation, a systematic inquiring experiment was carried out. In terms of the catalysts for methanation, we selected nickel as the active metal and γ -Al₂O₃ as the support due to its abundance and various advantages such as high stability and having a satisfactory porous structure. In order to examine whether Ni was successfully loaded on the support and observe the surface difference of the catalysts with diverse Ni loadings, N₂ isothermal adsorption/desorption, X-ray powder diffraction (XRD) and a scanning electron microscopy (SEM) were used to characterize the catalyst samples.

1 Experimental

1.1 Catalyst preparation

The Ni/ γ -Al₂O₃ catalysts with different Ni loadings (5%, 10%, 15% and 20%) were prepared by an impregnation method and the whole preparation process was elucidated as follows. First, the γ -Al₂O₃ granular support (2 to 3 mm) was impregnated with an aqueous solution of Ni(NO₃)₂ · 6H₂O. During the period of impregnation, the mixture was kept at 60 °C for 12 h so as to obtain catalyst precursor samples with uniformly dispersed Ni species. Secondly, after impregnation, all samples were dried at 120 °C overnight and subsequently calcined at 450 °C for 4 h in air. In order to describe the catalysts with different Ni loadings conveniently, the abbreviations of the catalysts are denoted as θ Ni/ γ -Al₂O₃ (θ = 5, 10, 15 and 20) in this paper.

1.2 Catalyst characterizations

The X-ray diffraction (XRD) analysis of the catalyst samples were measured on an X-ray diffractometer (Smart Lab, Japan) with Cu K α radiation under a 0.02° scanning step and a 20 (°)/min scanning speed operating at 40 kV and 100 mA. The wavelength λ was 0.154 nm and the scanning 2θ angle range was from 20° to 80°. The phase identification was carried out using the professional processing software Jade.

The specific surface area of the support and catalysts was evaluated by the BET method using N₂ adsorption at –196 °C via an automated gas adsorption analyzer (BELSORP-Mini, Japan). All the samples were pretreated under N₂ flow at 150 °C for 1 h prior to N₂ adsorption. The morphology of catalyst samples was determined by a HITACHI S-4800 scanning electron microscopy (SEM) operating at 5 kV.

1.3 Catalyst pretreatment and testing

The biomass gasification fuel gas methanation tests

were conducted in a continuous flow fixed-bed reactor equipped with a stainless steel tube (inner diameter: 50 mm) under atmospheric pressure (see Fig. 1). The cylinder gas was employed to simulate the composition of the biomass gasification fuel gas and the feed gas flow was controlled by the mass flowmeter. A peristaltic pump was employed to guide the water to the reactor tube. A pre-heater under 250 °C was utilized to preheat the feed gas and transform the liquid water into steam. The reaction temperature was measured in the middle of the cata-

lyst bed by a K-type thermocouple. In a typical methanation reaction, 50 mL catalysts were reduced in a gas flow of H_2 (GHSV: 1 000 h^{-1}) at 450 °C for 2 h. When the oven was cooled down to 200 °C, the reduction gas was subsequently switched to the reaction feed gas (GHSV: 2 000 h^{-1}). All the tests were performed in a temperature range of 300 to 500 °C. The composition of dry gaseous products was analyzed by VARIO PLUS (MRU, Germany) posterior to a water trap and the gas analyzer is accurate to the 0.01% level.

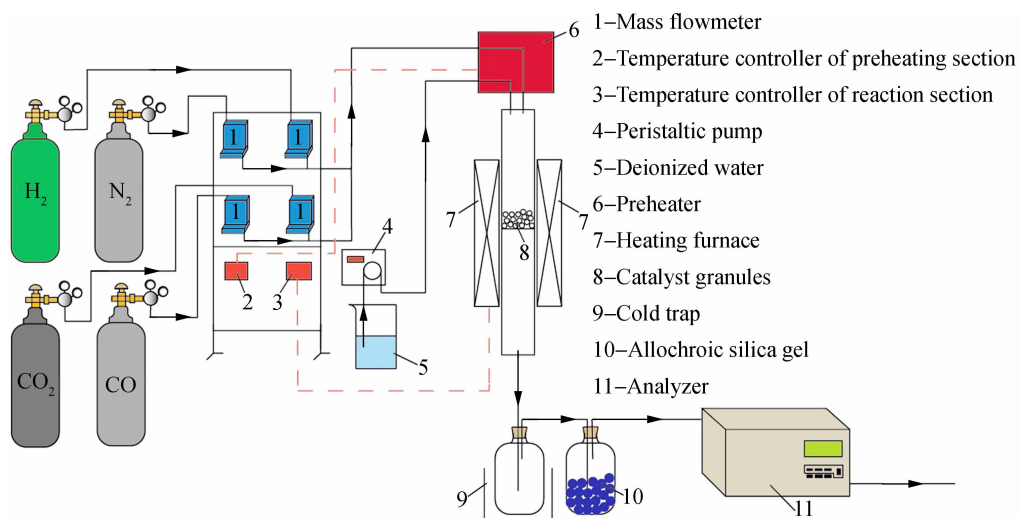
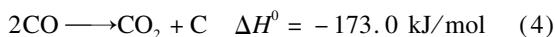
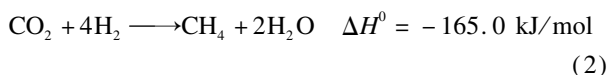
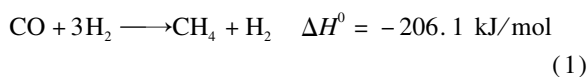


Fig. 1 Schematic diagram of biomass gasification fuel gas methanation reaction

1.4 Reactions and calculation

The process of biomass gasification fuel gas methanation possibly includes the following main reactions:



In light of the reactions above, the LHV of the biomass gasification fuel gas (unit: MJ/m³) is calculated as

$$LHV = 10.785V_{H_2} + 12.636V_{CO} + 35.914V_{CH_4} \quad (5)$$

The percentage conversion of CO (X_{CO}) and CH_4 product selectivity (S_{CH_4}) are determined by^[23]

$$X_{CO} = 100 \times ([F_{CO}]_{in} - [F_{CO}]_{out}) / [F_{CO}]_{in} \quad (6)$$

$$S_{CH_4} = \frac{100 \times [F_{CH_4}]_{out}}{[F_{CO}]_{in} + [F_{CO_2}]_{in} - [F_{CO}]_{out} - [F_{CO_2}]_{out}} \quad (7)$$

where V is the volume fraction and F is the molar flow rate of the inlet and outlet species.

2 Results and Discussion

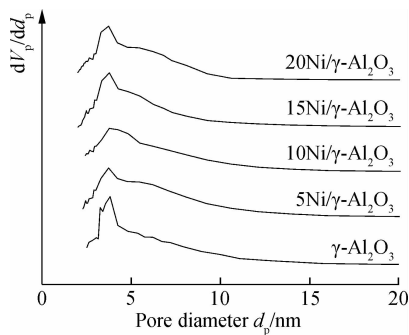
2.1 Textural properties and phase compositions of the catalysts

Tab. 1 exhibits the textural properties of the support and prepared catalysts. The $\gamma\text{-Al}_2\text{O}_3$ support is provided with a high surface area and pore volume. The addition of Ni can significantly decrease the BET surface area and pore volume. However, the shrunken surface area of the catalysts are still considerable enough for catalytic performance which can be proven in our following experiments. In addition, the pore volume and the average pore diameter descend with Ni loading. The pore size distribution and N_2 adsorption/desorption isotherms of the support and catalysts are shown in Fig. 2. It can be seen that the $\gamma\text{-Al}_2\text{O}_3$ support exhibits a pore size distribution centered at 3.82 nm. The addition of Ni to the support shifts the pore size distribution to smaller sizes. Most of the pore size concentrates on the range of 2 to 10 nm. Judging from the patterns of isotherms in Fig. 2(b), the $\gamma\text{-Al}_2\text{O}_3$ support and catalysts are with mesoporous structure (2 to 50 nm) according to the IUPAC classifications for the isotherms^[24].

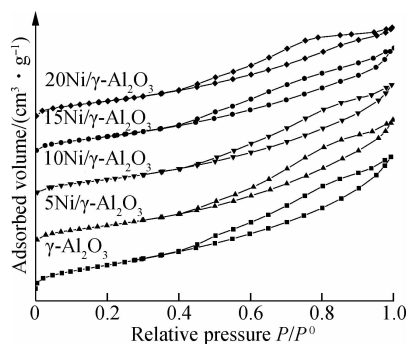
As shown in Fig. 3, in comparison with the material PDF cards, the diffraction peaks of four different Ni-load-

Tab. 1 Textural properties of the support and catalysts

Support/ Catalysts	Surface area/ (m ² · g ⁻¹)	Pore volume/ (cm ³ · g ⁻¹)	Peak pore diameter/nm	Average pore diameter/nm
γ -Al ₂ O ₃	241.46	0.399 5	3.82	6.618 0
5Ni/ γ -Al ₂ O ₃	192.70	0.367 3	3.72	7.624 6
10Ni/ γ -Al ₂ O ₃	179.80	0.337 8	3.72	7.515 3
15Ni/ γ -Al ₂ O ₃	179.15	0.314 4	3.71	7.020 2
20Ni/ γ -Al ₂ O ₃	175.66	0.275 4	3.71	6.270 2



(a)



(b)

Fig. 2 N₂ isothermal adsorption/desorption analysis. (a) Pore size distribution; (b) N₂ adsorption/desorption isotherms

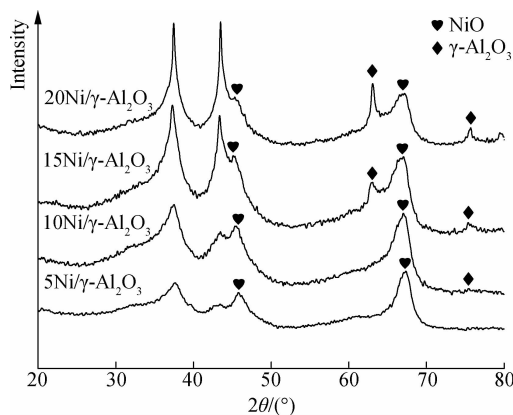
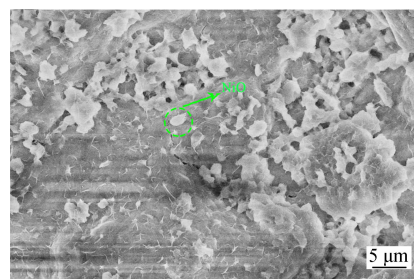


Fig. 3 XRD patterns of Ni/ γ -Al₂O₃ catalyst samples

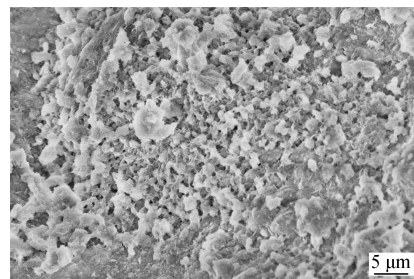
ing catalysts appeared at 37.3°, 43.3°, 62.9° and 75.5° are assigned to distinct peaks of the NiO (PDF # 75-0197). The XRD patterns of 5Ni/ γ -Al₂O₃ and 10Ni/ γ -Al₂O₃ catalysts do not show peaks at 62.9° and 75.5° due to the high dispersion of the NiO species. In addition, the unique peaks observed at 45.7° and 67.3° cor-

respond to distinct peaks of γ -Al₂O₃ (PDF #04-0880). These indicate that Ni was successfully loaded on the γ -Al₂O₃ carrier. Besides, Fig. 3 displays some discrepancy among four catalysts. It can be seen that the intensity of NiO diffraction peaks increases and half peak bandwidth decreases with the increase in Ni loading, which suggests that the grain size of NiO becomes larger when more Ni is loaded on the γ -Al₂O₃ support^[25]. This can be deduced by the Debye-Scherrer formula ($D = K\gamma/B\cos\theta$) and explained by the fact that overlarge Ni loadings will reduce the degree of NiO dispersion, thus easily leading to the aggregation of Ni species on the support.

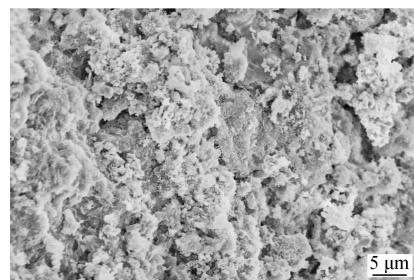
SEM images in Fig. 4 display the texture properties of four catalysts with different Ni loadings. It can be seen



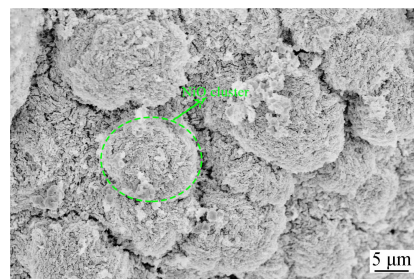
(a)



(b)



(c)



(d)

Fig. 4 SEM images of γ -Al₂O₃ supported Ni catalysts. (a) 5Ni/ γ -Al₂O₃; (b) 10Ni/ γ -Al₂O₃; (c) 15Ni/ γ -Al₂O₃; (d) 20Ni/ γ -Al₂O₃

that catalysts with less Ni loading (5Ni/ γ -Al₂O₃, 10Ni/ γ -Al₂O₃) show uneven structure while Ni species on the catalysts with more Ni loading (15Ni/ γ -Al₂O₃, 20Ni/ γ -Al₂O₃) disperse uniformly. Notably, a NiO cluster can be clearly observed in the SEM image of 20Ni/ γ -Al₂O₃, which is consistent with the XRD results.

2.2 Effect of reaction temperature

As shown in Fig. 5, the LHV of biomass gasification fuel gas can be increased to a various extent through methanation over Ni/ γ -Al₂O₃ catalysts (The dotted line in Fig. 5 represents the original LHV of biomass gasification fuel gas before methanation). All the catalysts with different Ni loadings presented catalytic performance and revealed the same changing pattern. For one certain catalyst, the LHV increases with the increase in reaction temperature to a peak then decreases. As for 5% and 10% Ni loading catalysts, the LHV reaches maximum at 400 °C while for the 15% and 20% Ni loading ones, the crest value of LHV appears at 350 °C.

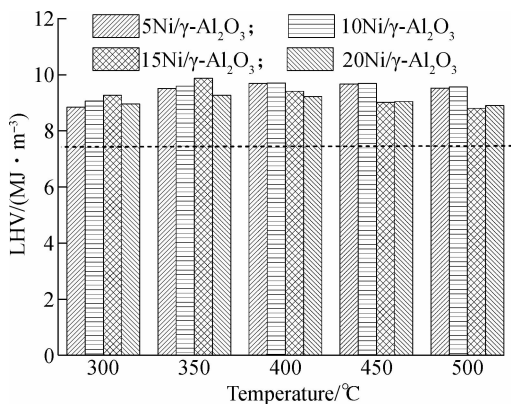


Fig. 5 LHV of biomass gasification fuel gas after methanation reaction with the dry feed gas consisting of 46.4% H₂, 18.6% CO, 27.0% CO₂, 8.0 % N₂ and the liquid water flow rate of 7.63 mL/h

The relationship between CO conversion and reaction temperature is displayed in Fig. 6. Notably, the line plots for all the catalysts reveal the same pattern. The CO conversion reaches a maximum value at 350 °C. Compared to other catalysts, 20Ni/ γ -Al₂O₃ has the highest CO conversion and 5Ni/ γ -Al₂O₃ has the lowest CO conversion. Tab. 2 lists the methane selectivity of the catalysts applied in the tests. As can be seen, the 15% and 20% Ni loading catalysts have the higher methane selectivity at 350 °C in contrast with other reaction temperatures. This might explain the fact that the LHV of biomass gasification fuel gas after methanation reaches a maximum value at 350 °C when combined with CO conversion, as shown in Fig. 6. However, in terms of 5% and 10% Ni loading catalysts, the methane selectivity at 400 °C is higher than those at other temperatures though the CO conversion at 400 °C is not the highest. Therefore, the LHV attains a crest value

at 400 °C.

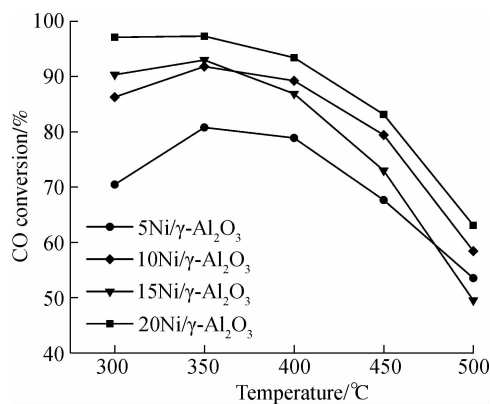


Fig. 6 CO conversion with the dry feed gas consisting of 46.4% H₂, 18.6% CO, 27.0% CO₂, 8.0% N₂ and the liquid water flow rate of 7.63 mL/h

Tab. 2 Methane selectivity of catalysts with different Ni loadings under test temperatures

Catalysts	* S ₃₀₀	S ₃₅₀	S ₄₀₀	S ₄₅₀	S ₅₀₀
5Ni/ γ -Al ₂ O ₃	54.03	52.73	77.03	56.91	63.47
10Ni/ γ -Al ₂ O ₃	48.15	59.16	69.83	47.31	48.79
15Ni/ γ -Al ₂ O ₃	64.53	77.51	59.99	50.63	59.64
20Ni/ γ -Al ₂ O ₃	59.06	60.75	48.87	46.90	48.78

Note: * represents the methane selectivity under 300 °C and the rest follow in the same manner.

2.3 Effect of H₂/CO ratio

As shown in Fig. 7, the LHV growth rate of biomass gasification fuel gas after methanation increases with the increase in the H₂/CO ratio. Best of all, the LHV of biomass gasification fuel gas can be improved by 34.3% when the H₂/CO ratio is 2.5 for 15Ni/ γ -Al₂O₃ catalyst. According to Eq. (1), the stoichiometric ratio of H₂/CO is 3, and from the perspective of reaction kinetics, more H₂ will promote the reaction. Therefore, the LHV has the largest growth rate when the H₂/CO ratio is 2.5 under the selected experimental conditions. Moreover, it can be seen that the LHV of biomass gasification fuel gas is difficult to enhance, it even decreases when the H₂/CO ratio is 0.8 or 1.0. This is due to the fact that under those circumstances, the H₂/CO ratio is far lower than the stoichiometric ratio of the methanation reaction. In consequence, the degree of the reaction is small and CH₄ production is insignificant. Hopefully, referring to the process of synthetic natural gas production from coal, adding a technology of water gas shift reaction (WGS) before methanation^[11] or developing bifunctional catalysts combined with WGS and methanation^[15] may be able to ease such a situation. For the 20Ni/ γ -Al₂O₃ catalyst, it is noteworthy that the LHV growth rate at the H₂/CO ratio of 2.5 is smaller than other catalysts. This phenomenon may be explained by the fact that powerfully released reaction heat will intensify the aggregation of the Ni species

and/or cause sintering, thus reducing the catalytic effect^[26]. According to SEM images in Fig. 4, 20Ni/ γ -Al₂O₃ catalyst presents a NiO cluster.

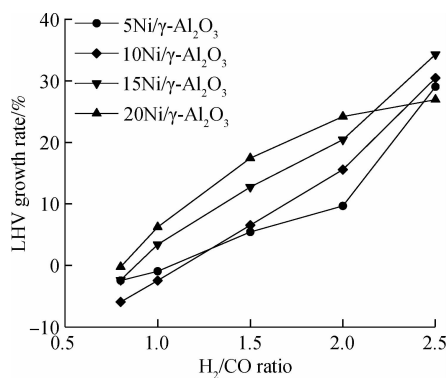


Fig. 7 LHV growth rate of biomass gasification fuel gas after methanation at 350 °C with the dry feed gas consisting of 27.0% CO₂, 8.0% N₂, the H₂/CO ratio varying from 0.8 to 2.5 and the liquid water flow rate of 7.63 mL/h

The lines in Fig. 8(a) show the varying pattern of CO conversion along with the change of H₂/CO ratio. Among them, 20Ni/ γ -Al₂O₃ catalyst has the the highest CO conversion and 5Ni/ γ -Al₂O₃ catalyst has the lowest. Similarly, the CO conversion increases with the increase in the H₂/CO ratio for all four catalysts with different Ni loadings. This phenomenon may be due to the fact that a larger H₂/CO ratio means more H₂ in the reaction system, thus providing more H₂ to react with the CO. In terms of CH₄selectivity (bar charts in Fig. 8(b)), 15Ni/ γ -Al₂O₃ possesses higher CH₄selectivity than 10Ni/ γ -Al₂O₃ although the CO conversion of 10Ni/ γ -Al₂O₃ is higher than 15Ni/ γ -Al₂O₃. The combined analysis of CO conversion and CH₄selectivity proves that the LHV growth rate using 15Ni/ γ -Al₂O₃ is higher than that using 10Ni/ γ -Al₂O₃ in the H₂/CO ratio range of 0.8 to 2.5.

2.4 Effect of water content

Biomass fuel gas derived during the gasification period generally contains impurities such as tar^[27], so washing is commonly employed in order to obtain pure gas product. In this case, dry fuel gas will carry various contents of water according to the washing temperature. In this paper, with the purpose of investigating the effect of water content on the LHV of biomass gasification fuel gas through methanation, several saturation water contents (6.2%, 8.1%, 10.4%, 13.4%, 17.2%) are adopted corresponding to different washing temperatures (45, 50, 55, 60 and 65 °C). As shown in Fig. 9, the LHV growth rate decreases with the water content for both the H₂/CO ratio of 2.5 (see Fig. 9(a)) and the H₂/CO ratio of 1.5 (see Fig. 9(b)), which indicates that introducing water into the system plays a negative role in enhancing the LHV of biomass gasification fuel gas.

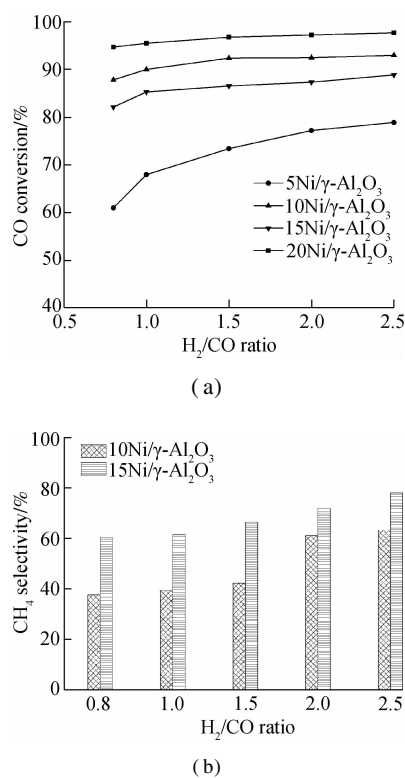


Fig. 8 Conversion and selectivity of the catalysts at 350 °C with the dry feed gas consisting of 27.0% CO₂, 8.0% N₂, the H₂/CO ratio varying from 0.8 to 2.5, and the liquid water flow rate of 7.63 m/h. (a) CO conversion; (b) CH₄ selectivity

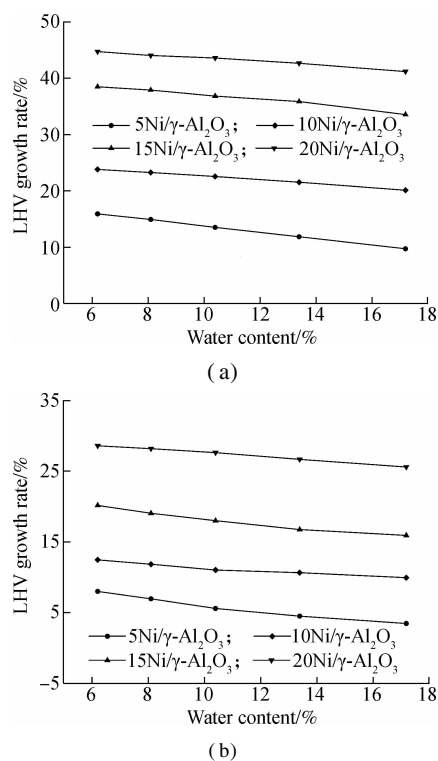


Fig. 9 LHV growth rate of biomass gasification fuel gas after methanation at 300 °C. (a) The dry feed gas consisting of 46.4% H₂, 18.6% CO, 27.0% CO₂ and 8.0% N₂; (b) The dry feed gas consisting of 39.0% H₂, 26.0% CO, 27.0% CO₂ and 8.0% N₂

CO conversion is influenced by water content as well. As can be seen in Fig. 10(a), CO conversion declines with water content for all four catalysts at the H_2/CO ratio of 2.5. This is due to the fact that water is the product of methanation reaction according to Eq. (1) and Eq. (2) and introducing water to the reaction system will increase the partial pressure of water, thus reducing the degree of methanation reaction. As a consequence, CO conversion decreases thereupon. Much attention should be paid on Fig. 11(a). For $15Ni/\gamma-Al_2O_3$ and $20Ni/\gamma-Al_2O_3$ catalysts, some difference in Fig. 10(a) can be seen. The CO conversion increases when the water content increases from 10.4% to 13.4%. This phenomena may be due to water gas shift reaction (WGS) according to Eq. (3). Ni also has a catalytic effect on WGS^[28]. When there are abundant Ni active sites for methanation, the extra Ni active sites can be utilized for WGS. This may explain the phenomena mentioned above since there are more Ni active species on the surface of $15Ni/\gamma-Al_2O_3$ and $20Ni/\gamma-Al_2O_3$ catalysts than that of $5Ni/\gamma-Al_2O_3$ and $10Ni/\gamma-Al_2O_3$ catalysts on the basis of the SEM images in Fig. 4. Besides, as mentioned in section 3.3, CH_4 selectivity of $15Ni/\gamma-Al_2O_3$ catalyst is higher than that of $10Ni/\gamma-Al_2O_3$ catalysts (bar charts shown in Fig. 10(b) and Fig. 11(b)) though the CO conversion of $15Ni/\gamma-Al_2O_3$ catalyst is lower than that of $10Ni/\gamma-Al_2O_3$ catalyst, which

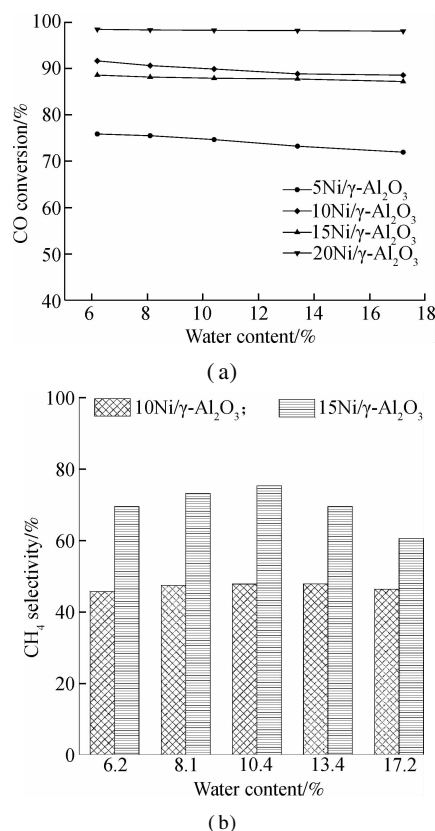


Fig. 10 Conversion and selectivity of the catalysts at 300 °C with the dry feed gas consisting of 46.4% H_2 , 18.6% CO , 27.0% CO_2 and 8.0% N_2 . (a) CO conversion; (b) CH_4 selectivity

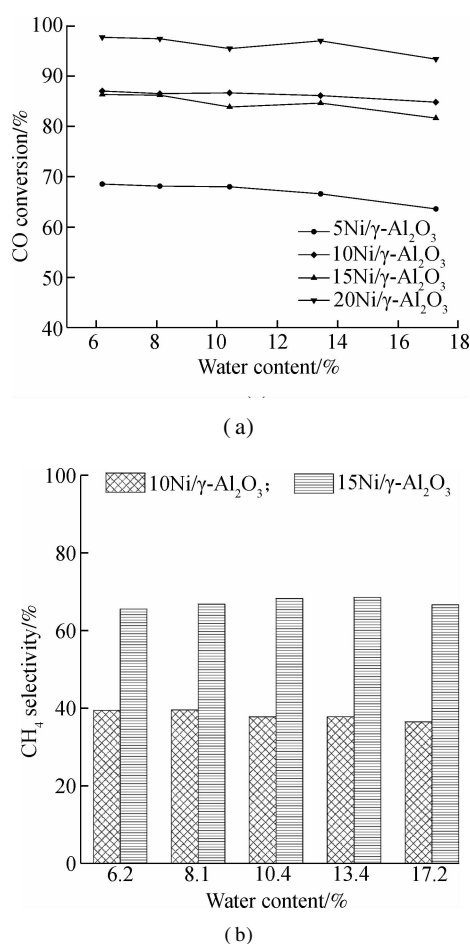


Fig. 11 Conversion and selectivity of the catalysts at 300 °C with the dry feed gas consisting of 39.0% H_2 , 26.0% CO , 27.0% CO_2 and 8.0% N_2 . (a) CO conversion; (b) CH_4 selectivity

leads to the fact that the LHV growth rate using $15Ni/\gamma-Al_2O_3$ catalyst surpasses the LHV growth rate using $10Ni/\gamma-Al_2O_3$ catalyst.

3 Conclusion

1) The LHV of biomass gasification fuel gas can be heightened to various degrees with the catalysis of $Ni/\gamma-Al_2O_3$ under distinct operation conditions. According to the performance tests, $15Ni/\gamma-Al_2O_3$ and $20Ni/\gamma-Al_2O_3$ are highly efficient in terms of improving the LHV of biomass gasification fuel gas due to their remarkable catalytic effect.

2) When investigating the single influential factor, $15Ni/\gamma-Al_2O_3$ and $20Ni/\gamma-Al_2O_3$ catalysts function desirably at 350 °C due to their satisfactory CO conversion and CH_4 selectivity. Also, a higher H_2/CO ratio and lower water content are favorable for elevating the LHV of biomass gasification fuel gas.

3) From the results of the experiments, improving the LHV of biomass gasification fuel gas with a low H_2/CO ratio (<1.0) merely through methanation is difficult to achieve. Adding a process of water gas shift reaction before methanation or employing catalysts with both func-

tions may address such a problem.

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Ni/ γ -Al₂O₃ 甲烷化催化剂提高生物质气化燃气低位热值的实验

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摘要:制备了负载于 γ -Al₂O₃ 载体上的镍基甲烷化催化剂用于提高生物质气化燃气的低位热值. 在性能测试之前,采用氮气等温吸附/脱附、XRD 和 SEM 等方法对催化剂样品进行表征. 一系列催化性能测试表明,在提高生物质燃气低位热值方面,负载量为 15 % 和 20 % 的镍基催化剂较负载量为 5 % 和 10 % 的镍基催化剂具有更优越的催化甲烷化性能. 此外,反应温度、H₂/CO 比和含水量等可控影响因素在生物质燃气甲烷化过程中影响很大. 15Ni/ γ -Al₂O₃ 和 20Ni/ γ -Al₂O₃ 催化剂在 350 ℃ 时具有更高的 CO 转化率和 CH₄ 选择性并且在此温度下生物质燃气的低位热值增长率可达 34.3 %. 综合考虑 CO 转化率和 CH₄ 选择性,由于较高的 H₂/CO 比和较低的含水量有利于提高甲烷化的反应程度,因此,增大 H₂/CO 比和降低含水量有利于提高生物质燃气的低位热值.

关键词:镍基催化剂;甲烷化;生物质燃气;低位热值

中图分类号:O643.3