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Preparation of Ni-La/Al₂O₃-CeO₂-Bamboo charcoal catalyst and its application in co-pyrolysis of straw and plastic for hydrogen production

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Abstract

The developed Ni-La/Al₂O₃-CeO₂-Bamboo charcoal (ACB) catalyst was applied to the co-pyrolysis of straw and plastic to produce hydrogen in a horizontal quartz tube pyrolysis furnace. In this study, the effects of the mixing ratio of straw and plastic, the presence and stability of the catalyst on the co-pyrolysis hydrogen production were investigated. Experiment showed that the addition of PE can increase the yield of H₂ within a certain range, and the best mass ratio of 5:5 was found. In the co-pyrolysis process with the participation of the catalysts, the macromolecular tar can be cracked into combustible gases such as H₂, and the H₂ yield could be increased to 332.2ml/g (Ni-La/ACB) is much higher than 68.87ml/g without catalyst. Compared with Ni/ACB, Ni-La/ACB had been increased the alkalinity by adding La element and enhanced the carbon deposition resistance of the catalyst, which makes the catalyst maintain higher stability. This was also confirmed in stability test experiments.

Keywords: Composite support· Co-pyrolysis· Catalyst· Hydrogen yield· Catalytic performance ·

Introduction

The depletion of fossil energy reserves is driving people to search for alternative energy¹. Biomass is considered to be one of the materials that can replace or supplement the traditional fossil energy structure due to its richness, sustainability and environmental protection characteristics 2-5. Biomass contains C and H, which determines the feasibility of converting biomass into fuels of the same quality as fossil energy. As a renewable energy source, biomass is cleaner and less polluting than traditional forms of energy. The carbon neutralization process can be achieved when biomass is used to provide energy. Pyrolysis is a promising thermochemical conversion

method that can convert low-value biomass into high-quality fuels and other value-added products⁶. In the absence of oxidants, pyrolysis uses heat to degrade raw materials into mixed gas, which mainly contains H₂, CO, CO₂, CH₄ and C_nH_m⁷⁻⁹. Straw is a common agricultural waste, converting it into fuel through pyrolysis not only help alleviate the soaring environmental issues, but also reduce fossil fuel consumption to meet the ever-increasing energy demands¹⁰.

However, a large amount of coke will be produced in the process of straw pyrolysis. Adding hydrogen-rich co-reactants such as plastics can reduce the formation of coke and obtain energy¹¹⁻¹³. To the best of our knowledge, the proportion of plastics in municipal solid waste (MSW) reaches 15%-20%. Degrading plastics through pyrolysis is also a more environmentally friendly method^{14,15}. The plastics can be efficiently decomposed by pyrolysis to produce hydrogen within a few minutes. The high H/C ratio of plastics can balance the high oxygen content of straws compared to only pyrolyzing plastic or straw. But the plastic pyrolysis product incompletely decomposed will stick to the surface of the reactor. Catalytic pyrolysis can solve the above problems¹⁶. The co-pyrolysis of plastic (zero oxygen content) and straw can not only promote the maximum decomposition of raw materials and reduce the coke yield, but also achieve higher hydrogen production and lower tar yield¹⁷⁻¹⁹. In the mixed gasification experiment of PE (polyethylene) and wood chips, the yield of syngas, H₂ and hydrocarbons reached the highest value when the percentage of the PE is about 80wt%²⁰. When wood chips are co-gasified with PP (polyethylene), HDPE (High Density Polyethylene), PS (Polystyrene) separately, the highest gas yield is obtained when wood chips are co-gasified with PP. The H₂ concentration increased from 30.3% to 36.1% with the PP content increased from 0 to 20wt% in co-pyrolysis processes²¹. Lopez et al.²² studied the effect of HDPE on the steam gasification of biomass in a spouted bed reactor. The results showed that with the increase of HDPE content, the gas production increased and the tar production rate decreased. When the proportion of HDPE is 0wt%, 25wt% and 50wt%, the tar content is 58.2 g/Nm³, 32.0 g/Nm³, 9.7 g/Nm³ respectively at 900°C. During this process, the maximum concentration of H₂ increased to 57%.

Recently, catalysts such as carbonaceous compounds and metal oxides have been intensively researched and developed for Pyrolysis. Efficient catalytic activity was exhibited because of its large surface area, large porosity, good mechanical properties and stability²³. Guo et al.²⁴ used RHC (rice husk char) and metal (Fe, Cu, and K)

impregnated carbon to catalyze biomass pyrolysis. The catalyst showed high tar conversion efficiency of 77.1% for RHC, 82.7% for K-RHC, 90.6% for Cu-RHC and 92.6% for Fe-RHC at 800 °C. The char and char-supported catalyst promote the conversion of larger polycyclic aromatic hydrocarbons into lighter tar compounds, which are further catalyzed and converted into small molecular gas compounds [25-28]. Five Ni/C catalysts with different Ni content were tested [29], the sample with 13.2wt% Ni showed the highest conversion of CH₄ for dry reforming of methane at 800°C. The yield of 31.4 vol% for H₂. After 6 hours of operation, the catalyst activity is relatively stable. The advantage of the carbonaceous support is that it can resist catalyst deactivation due to coke deposition. The morphology of the carbon material can promote mass transfer around the active site. The effects of catalysts Ni-CaO-C and Ni/Al₂O₃ on the mixed pyrolysis of pine wood and plastic were studied as well [30,31]. With the addition of 30wt%-40wt% plastic, the H₂ yield was obtained using Ni-CaO-C as the dual-support catalyst is much higher than that of using the traditional catalyst Ni/Al₂O₃. Carbon, which displays a rich pore structure to provide sufficient surface area, is ideal catalyst support.

Nickel-based catalysts have been widely used in pyrolysis due to their excellent tar cracking and reforming properties [15, 32,33]. However, they tend to be rapidly deactivated due to the accumulation of carbon deposits during the pyrolysis process. Taking these into account, nickel-based catalysts can be modified by adding rare earth elements to improve performance. A CeO₂ modified Ni/Al₂O₃ and a MgO modified Ni/Al₂O₃ catalyst were successful reported by Santamaria et al [34]. The initial activities of the catalysts were similar. With the addition of CeO₂, which was used as a promoter, the stability of the catalyst greatly improved because it enhanced gasification of coke precursors. The CeO₂ structure has highly movable vacancy oxygen sites, reducing the degree of carbon deposition. What's more, reports [35-37] show that the addition of precious metals such as Ce, La and Co [38] can reduce the degree of coking of Ni-based catalysts and improve the dispersibility of active metals. Zhang et al. [39] used urea hydrolysis to synthesize a series of La-doped Ni-Mg/Al catalysts with different lanthanum loading. During the study of the service life of the catalyst, they found that the NiLa5 catalyst showed stable activity even after 150 hours of operation. Ce or La was introduced to prepare a modified Cu-SAPO-34 catalyst [40]. The modified catalyst can effectively inhibit the aggregation of Cu components, significantly improve the stability of Cu-SAPO-34, and further maintain a relatively

large specific surface area and uniform pore size distribution.

Considering the above information mentioned. The focus of this work has been developed an efficient catalyst for hydrogen production by co-pyrolysis of straw and plastics. Composite support ACB ($\text{Al}_2\text{O}_3\text{-CeO}_2\text{-Bamboo charcoal}$) was synthesized by co-precipitation, and Ni/ACB and Ni-La/ACB catalysts have been prepared on ACB. The effects of straw /PE ratio, the presence and stability of catalyst on the H_2 yield during co-pyrolysis were described.

Experimental

Materials

The raw materials for the pyrolysis experiment were soybean straw and PE powder, which came from Shanxi Province and Wuhan City, Hubei Province, respectively. Soybean straw is crushed to about 40 mesh particles, and then the crushed particles are dried in a drying oven at 105 °C for 24 hours to eliminate the influence of moisture in the pyrolysis experiment. PE powder purchased is 40 mesh, and it is also dried for 24h after pretreatment. The dried materials are sealed and stored for later use. The waste bamboo wood was selected from Wuhan city, China. it was first dried naturally, then crushed and sieved to particles of about 0.45 mm. Among the above materials, bamboo wood is used to prepare bamboo charcoal carrier, soybean straw and PE are used as materials for hydrogen production by pyrolysis. The proximate and ultimate analysis of soybean straw and PE powder are listed in Table 1. The higher the volatile content in the raw material, the less coke produced. PE only contains C and H, and the content of O in straw is relatively high.

Table 1 Proximate and ultimate analysis of soy straw and PE

Materials	Ultimate Analysis (wt%)					Proximate Analysis (wt%)			
	C	H	O*	N	S	M _{ad}	A _d	V _{ad}	FC _{ad}
Soybean Straw	41.08	5.53	52.15	1.24	0	4.6	8.7	82.06	4.64
PE	85.78	14.22	-	-	-	-	<0.05	99.95	-

M (moisture); A (ash); V (volatile); FC (fixed carbon);

* Calculated by difference; ad, on air dried basis; d, on dry basis.

Catalyst preparation

Bamboo charcoal was obtained by high-temperature pyrolysis of bamboo powder. The reactor temperature was raised from room temperature to 800 °C at a rate of 10 °C/min under nitrogen atmosphere and kept at 800 °C for 2 h.

The composite support ACB (Al_2O_3 - CeO_2 -Bamboo charcoal) was prepared by co-precipitation method. A certain amount of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Bamboo charcoal and deionized water were added to a 500 mL beaker and stirred vigorously on a magnetic stirrer until all the substances were dissolved. Then ammonia water (25%) was added to the beaker with stirring to adjust the pH value of the solution. stopping adding ammonia water When $\text{pH} = 9$ and continuing stirring for 3 h to complete the precipitation process. The mixed solution was left standing at room temperature for 6 h, and the solution after standing was dried to obtain support precursor. Finally, the support precursor was heated to 800 °C in a tube furnace under a nitrogen atmosphere and kept at 800°C for 3h to obtain ACB. The molar ratio of each component in the composite support is 1:1:1.

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was used as the precursor of Ni, and 10wt% of Ni was designed to load on ACB. Ni/ACB catalyst was prepared by a homogeneous precipitation method. First, ACB, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{CO}(\text{NH}_2)_2$ were fully dissolved into deionized (DI) water. Stirring the mixture evenly on a magnetic stirrer at room temperature. Then transfer the mixture to a 500ml round bottom flask, The blend was reacted in an oil bath at 115 °C for 2h, resulting in the precursor deposited on the support. After the reaction was complete, the mixture filtered and washed until it became neutral, then dried overnight. Finally, the product dried was calcined in a nitrogen atmosphere at 750 °C for 2h to obtain a Ni/ACB catalyst. In order to investigate the effect of the addition of active component La on the catalytic performance of the Ni/ACB catalyst. $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was selected as the La precursor, and the designed addition amount of La was 10 wt%.

Apparatus and process

The experimental device is shown in Fig.1, including a gas supply system, a pyrolysis reactor, a gas collecting bag, a gas purification device and an analysis system. The co-pyrolysis experiment was carried out in a horizontal quartz tube pyrolysis furnace. The biomass and the catalyst were placed in quartz boats, and the quartz boat was placed in the quartz tube, and the quartz tube reactor was 60 mm in diameter and 1200 mm in

length.

The quartz boats containing the catalyst and biomass are put into the pyrolysis furnace, and the flanges on both sides are closed. First, nitrogen is used to purge the air in the furnace for 20 minutes to ensure an oxygen-free environment. After the pyrolysis furnace is heated from room temperature to the set temperature (700°C), the materials are quickly sent into the high temperature zone. The raw materials rapidly decompose at high temperature and the volatile matter is in full contact with the catalyst. After the reaction time is over, the gas valve is opened, and the gas is collected into the gas collecting bag through the pipe. Finally, the gas passes through the ice-water condenser of the pretreatment system and enters the gas analyzer after being dried to determine the gas composition and content, and record the experimental data. The duration of each experiment was the same, and repeated experiments were carried out to ensure the reproducibility of the process.

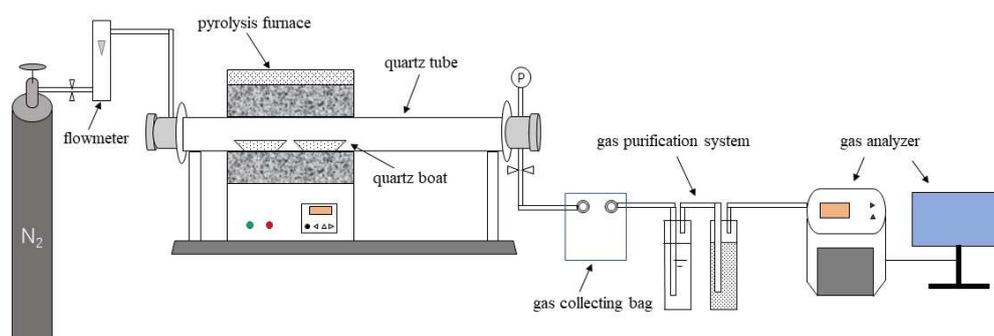


Fig.1 Schematic diagram of the experimental process

Results and discussion

TG analysis of materials

Fig.2 shows the TG and DTG curves obtained from the pyrolysis of soybean straw, PE, soybean straw, and PE. The decomposition zone of soybean straw could be divided into three stages. The first stage is the physical dehydration stage and ends at about 180°C. This stage is mainly due to the hygroscopicity of soybean straw, and the weight loss is small; the main decomposition stage occurs at about 180°C to 550°C, and the total weight loss can reach 60wt%. There is a strong peak near 330 °C, which may be caused by the pyrolysis of cellulose and hemicellulose [41]; in the third stage, the straw has no major weight loss and basically remains stable. PE had no obvious weight loss in the early stage, indicating that there are no volatile substances such as moisture in the raw

materials. The weight loss starts when the temperature rises to 420°C, and the maximum weight loss peak appears at 490°C. The entire pyrolysis process is divided into two stages and only one weight loss peak appears, As reported by other researchers [42]. The residual amount is less than 5%. For the mixture of straw and PE, as the test temperature rises, the weight loss is increasing. A large weight loss peak appears around 480°C, and the maximum mass loss reaches 88wt%. Therefore, the temperature at which soybean straw starts to decompose is lower, but the pyrolysis rate of PE is higher than that of straw, and the amount of residual carbon after PE pyrolysis is much smaller than that of straw.

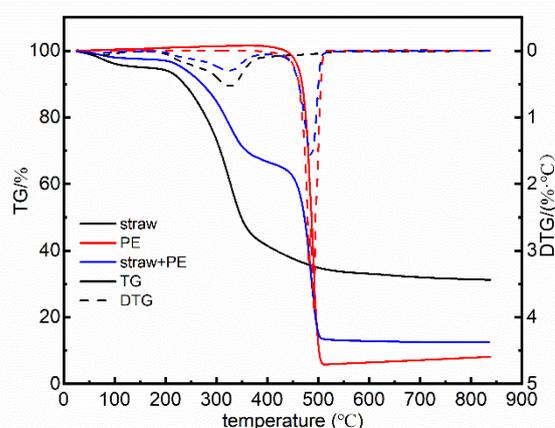


Fig .2 TG and DTG analysis of straw, PE, straw+PE

TG and BET analysis of support

Fig.3 and Table 2 are the thermogravimetric curve diagram and the BET analysis of the carrier separately. TG analysis on support to determine the thermal stability. Fig.3 shows the TG analysis of ACB. It could be seen from the TG and DTG curves that the drying stage of ACB was before 150 °C, there was a large weight loss at this stage . After that, it basically remained stable. The weight loss was less than 10%, indicating that the thermal stability is good and can provide more stable support for the catalyst. The specific surface area of the ACB was analyzed, and the result is shown in Table 2. The composite support prepared by the co-precipitation method has a larger specific surface area. The larger specific surface area enables the active ingredient to be more uniformly dispersed on the surface of the support, avoiding the agglomeration of the active ingredient [43,44].

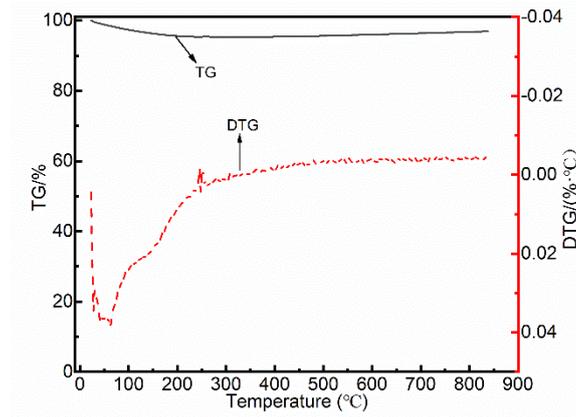


Fig .3 Thermogravimetric analysis of support

Table 2 BET analysis of supports

Sample	surface area $A/(m^2 \cdot g^{-1})$
ACeB	82.29

XRF analysis of support and catalysts

Table 3 shows the composition and percentage content of ACB support, Ni/ACB and Ni-La/ACB catalysts. XRF shows that the relative mass fraction ratio of Al_2O_3 and CeO_2 in ACB is 0.53, which is lower than the theoretically calculated value of 0.59 (converted at a molar ratio of 1:1). The active components Ni and La form NiO and La_2O_3 under high temperature calcination respectively. The theoretical design amount of NiO is 12 wt% (calculated according to the design load of Ni 10 wt%), and the theoretical design amount of La_2O_3 is 20 wt% (calculated according to the design load of La 10 wt%). During the calcination of the catalyst, the surface of the original support changes and the substances loaded on its surface decompose. Moreover, XRF mainly analyzes the microscopic area of the catalyst surface, which will lead to deviation between the test value and the theoretical value.

Table 3 XRF analysis of the support and catalysts

sample	Main composition and content (wt%)				
	Al_2O_3	CeO_2	NiO	La_2O_3	Others
ACB	33.50	62.90	–	–	3.6
Ni/ACB	26.24	53.17	16.90	–	3.69
Ni-La/ACB	19.92	41.84	17.62	18.33	2.29

XRD analysis of catalysts

Fig.4 shows the XRD pattern of the catalysts. Due to support is composite, the diffraction peaks of CeO_2 and Al_2O_3 can be seen in the figure, which is consistent with the results of XRF. It can be seen from Fig.4 that NiO particles are detected at $2\theta=37.3^\circ$, 43.3° , and 63.5° , which is similar to other reports [45]. This shows that in the Ni/ACB catalyst, the active component is mainly NiO. With the La was added, the characteristic peaks of La_2O_3 appear as well as the characteristic peaks of Ni. It can be considered that part of NiO is reduced to Ni element after La element is added.

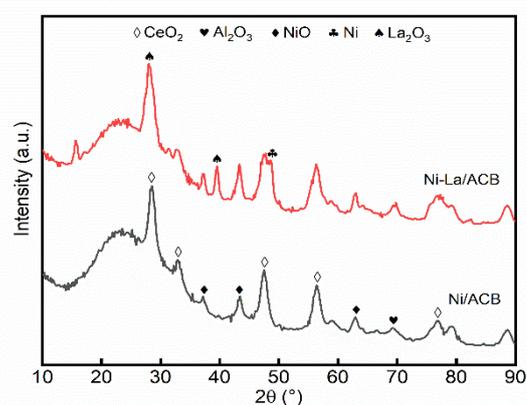


Fig.4 XRD patterns of catalysts: Ni/ACB and Ni-La/ACB

SEM-EDX analysis of catalysts

As shown in Fig.5, the apparent morphology of catalysts is observed by SEM. Fig.5(a) shows that the Ni/ACB presents a staggering flake structure, Ni is uniformly dispersed on the flake layer. After adding the auxiliary La, the flaky structure changed into Staggered structure, and metal dispersibility is further improved on the surface. As an auxiliary, La has a promoting effect on improving the structure of catalyst and improving the dispersibility of the metal on the surface [46] The EDX spectrum on the right is an analysis of the substances in the catalyst. A large number of diffraction peaks of Al, Ce, Ni and La can be seen from the EDX figure, which also indicates that the active component is well combined with the carrier. These characterization results confirm the above characterization results again.

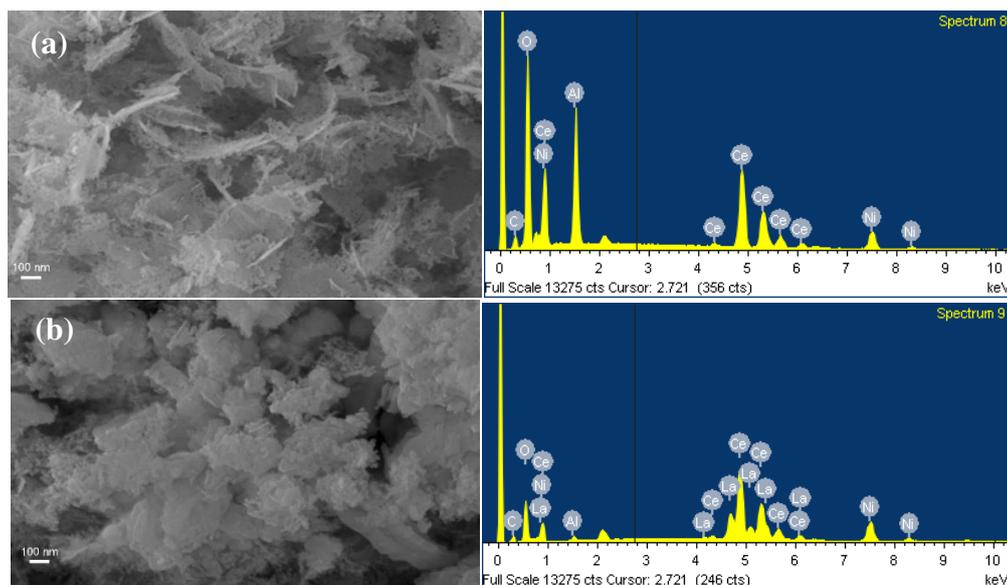


Fig.5 SEM-EDX images of catalysts: (a) Ni/ACB and (b) Ni-La/ACB

Co-pyrolysis experiment

Influence of straw/PE ratio

In order to explore the effect of PE addition on pyrolysis gas production, the straw/PE ratio was varied in the range of 10:0-0:10. The pyrolysis experiment was carried out without catalyst and the pyrolysis temperature was 700 °C. The results are shown in Fig.6. With the increase of PE, the output of H₂ showed a trend of first increasing and then decreasing. When the mass ratio of straw/PE was 5:5, the highest H₂ yield is 68.87 ml/g. PE mainly contains C and H elements. Increasing the proportion of PE in the feedstock led to enhance the production of total gas, especially the production of H₂ and CH₄, while CO and CO₂ were decreased due to the decrease of O content in the feedstock. Therefore, the mixed pyrolysis of straw and plastic has a significant synergistic effect on gas production. The bimetallic Ni-Fe@CNF/PCs catalyst to catalyze the pyrolysis of biomass and waste plastics was reported [47]. Biomass/plastic ratio of 0.5 was found for a catalyst to play best roles in the H₂-rich syngas quality, and the H₂ yield is as high as 33.66 mmol H₂/g biomass. In the following experiments, the mass ratio of straw/PE is 5:5.

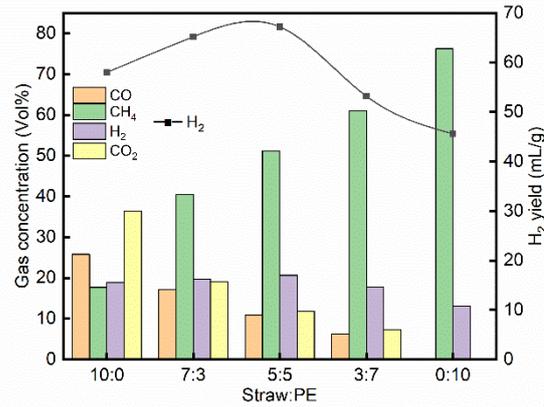


Fig.6 Gas production when changing Straw/PE ratio (Temperature:700°C)

Influence of catalyst

Fig.7 shows the effect of different catalysts on straw and PE co-pyrolysis. Biomass pyrolysis will produce char (tar) and gas without catalyst. As shown in Fig.7, the H₂ concentration is only 20.65 vol% without catalyst, while the CH₄ concentration rises to 51.12 vol%. The H₂ concentration upgrades significantly under the action of catalysts, and it can reach up to 56.4 vol%(332.2ml/g). Catalysts participate in the following reactions (Eqs. (1)-(7)) [7]. Methane cracking and reforming reactions and tar reforming reactions are promoted by catalysts, so that the macromolecular compounds are decomposed into small molecular substances, and the hydrocarbons are cracked into H₂ and CO to obtain more high-value gases.



With catalyst, the content of H₂ has increased intensely, CH₄ and CO₂ content have marked decreased, CO content have increased slightly. According to Eq. (6), in the dry reforming reaction of tar, hydrocarbons combine with CO₂ to converted into H₂ and

CO. The H₂ yields are 307.6 ml/g and 332.2 ml/g in the presence of catalysts, respectively, which are much higher than the hydrogen yield without catalyst (68.87ml/g). It can be summed up that, under the same experimental conditions, Ni-La/ACB played the best roles in the co-pyrolysis to produce hydrogen.

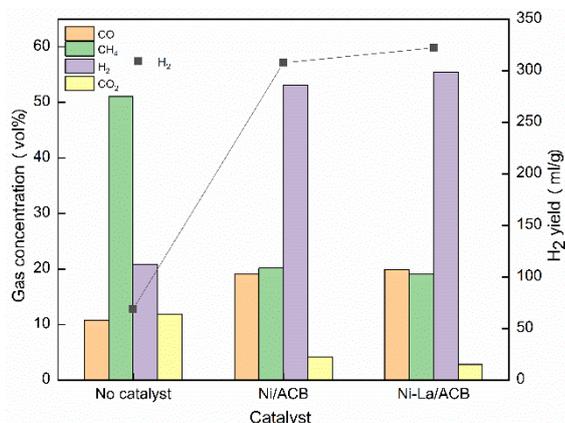


Fig.7 Influence of different catalysts on gas yield (Temperature:700°C, Straw/PE:5: 5)

Stability test of catalysts Ni /ACB and Ni-La/ACB

Under the same operating conditions as mentioned above, the stability of Ni/ACB and Ni-La/ACB were investigated. In order to further compare the hydrogen production effect of co-pyrolysis and straw pyrolysis alone. The stability of the catalyst in the pyrolysis of straw for hydrogen production was also studied. And the results are shown in Fig.8.

Fig.8(a) shows the hydrogen production of straw pyrolysis, and Fig.8(b) shows the hydrogen production of straw and PE co-pyrolysis. It could be seen that the H₂ concentration by pyrolysis with catalyst is higher than that without a catalyst. With the addition of La, the H₂ content improves again, which largely depends on the increase in the alkalinity of Ni-La/ACB catalyst, and the carbon deposition resistance and stability are enhanced simultaneously [48]. Comparing (a) and (b) once again proves that adding plastic can increase the concentration of H₂.

Fig.8(b) shows that the hydrogen production increased from 20.65 vol% without catalyst to around 55 vol% with catalysts, and the maximum can reach 56.4 vol%(Ni-La/ACB). Ni/ACB have a faster deactivation rate in the process of co-pyrolysis. The C/H ratio in PE is about 5.67, and it is reported in the literature [49] that the products of polyolefin pyrolysis are mainly long-chain alkanes and olefins. Barbarias et al. [50] analyzed the influence of the pyrolysis process of different plastic models on catalyst deactivation. Through experiments, it is concluded that the coke and compounds

deposited on the surface of the catalyst after pyrolysis block the Ni active sites. Compared with straw pyrolysis, there will be more carbon deposits in co-pyrolysis. And the pores and acid sites on the catalyst surface will be blocked, which will prevent the contact between volatile and active components. From Fig.8(b), the deactivation rate of Ni-La/ACB is lower than that of Ni/ACB. This was mainly due to the fact that doping with La can significantly enhance the anti-carbon ability of the catalyst and improves the stability. At the same time, the support's larger specific surface area and better thermal stability also provide a good foundation for the catalyst. Compared with chart (a), in co-pyrolysis experiment, the H₂ concentration was 30.8 vol% (Ni/ACB) and 42.52 vol% (Ni-La/ACB) after 6 experiments, respectively.

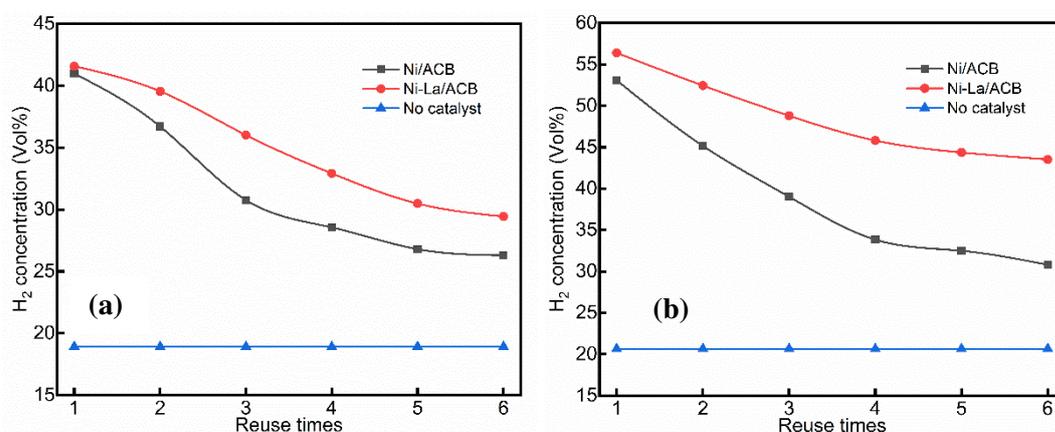


Fig.8 Stability of Ni/ACB and Ni-La/ACB in hydrogen production by pyrolysis: (a) Straw, (b) Straw+PE (Temperature:700°C, Straw/PE:5: 5)

Conclusions

In the present work, the co-pyrolysis of straw and PE was investigated in a horizontal quartz tube furnace using nickel-based catalysts on carbon composite supports. Related experiments have been performed to explore the effects of the straw/PE mass ratio, catalytic type and stability on the yield of hydrogen. The experimental data shows that co-pyrolysis can increase the yield of hydrogen and the conversion rate of hydrocarbons. The highest H₂ yield of 332.2ml/g is obtained with Ni-La/ACB catalyst at straw/PE ratio of 5:5 at 700°C. The catalyst can also maintain the highest stability:

- (1) Through experimental exploration, it is concluded that when straw and plastic are co-pyrolyzed to produce hydrogen, adding an appropriate amount of PE will help increase the H₂ output. With the increase of the proportion of plastic in the pyrolysis, the H₂ yield will increase first and then decrease. When the straw/PE ratio is 5:5, the maximum H₂ yield value is 68.87 ml/g;

- (2) The presence of the catalyst has played a significant role in promoting the production of hydrogen in co-pyrolysis. The H₂ yield were 307.6 ml/g (Ni/ACB) and 332.2ml/g (Ni-La/ACB) with catalysts. Indicating that the Ni-La/ACB has the best catalytic performance and can effectively increase the yield of H₂.
- (3) It can be seen from stability tests that the deactivation rate of Ni-La/ACB is slower than that of Ni/ACB. This may be due to the larger specific surface area provided by the support, and the addition of La made the active metal more dispersed on the support surface. Moreover, the alkalinity of the catalyst was increased to some extent, and the deposition of carbon on the catalyst surface was weakened. The stability of Ni-La/ACB in the co-pyrolysis experiment was the best. After 6 experiments, the H₂ concentration was only reduced from the initial 56.4 vol% to 42.52 vol%.

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Conflict of interest These authors declare that they have no known financial interests.

Consent for Publication All authors agree to publish this article in BioEnergy Research.

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