Preparation of Ni-La/Al$_2$O$_3$-CeO$_2$-Bamboo Charcoal Catalyst and Its Application in Co-pyrolysis of Straw and Plastic for Hydrogen Production

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Abstract
The conversion of biomass and plastic into hydrogen through catalytic pyrolysis is a promising technology for the production of clean fuels. The developed Ni-La/Al$_2$O$_3$-CeO$_2$-Bamboo charcoal (ACB) catalyst was applied to the co-pyrolysis of straw and polyethylene (PE) to produce hydrogen. This research explored the optimal mixing ratio of straw and PE, and the influence of the presence and stability of the catalysts on hydrogen production. Experiments show that the best mixing ratio is 5:5. Ni-La/ACB can significantly promote the production of $\text{H}_2$ (13.56 mmol/g), and it can still maintain high stability after repeated use, which is inseparable from the introduction of La to improve the performance of the catalyst. It can be concluded that adding a certain proportion of plastic is beneficial to increase $\text{H}_2$ production, and co-pyrolysis can solve the pollution problem caused by improper treatment of plastics while making full use of renewable energy.

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

Introduction
The depletion of fossil energy reserves is driving people to search for alternative energy [1]. 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 by thermochemical processes [6]. Pyrolysis is a promising thermochemical conversion method that can convert low-value biomass into high-quality fuels and other value-added products [7]. In the absence of oxidants, pyrolysis uses heat to degrade raw materials into mixed gas, which mainly contains $\text{H}_2$, CO, CO$_2$, CH$_4$, and C$_n$H$_m$ [8–10]. Straw is a common agricultural waste, converting it into fuel through pyrolysis not only helps alleviate the soaring environmental issues, but reduces fossil fuel consumption to meet the ever-increasing energy demands [11].

However, a large amount of tar will be produced during the pyrolysis of straw, and the conversion rate of biomass is low at this moment. Adding hydrogen-rich co-reactants (such as waste plastics) can change the distribution of pyrolysis products through the synergy of the two [12–14]. To the best of our knowledge, plastics account for a high proportion of municipal solid waste (MSW). Meanwhile, ordinary combustion treatment methods generated a large amount of polycyclic aromatic hydrocarbons, which will cause a series of serious environmental pollution problems [15, 16]. Degrading plastics through pyrolysis is also a more environmentally friendly method [17, 18]. The plastics can be efficiently decomposed by pyrolysis to produce hydrogen within a few minutes. Compared with the pyrolysis of straw or plastic alone, the high H/C ratio of plastic can balance the high oxygen content of straw, which results in higher hydrogen production and lower tar production [19]. But the plastic pyrolysis product incompletely decomposed will stick to the surface of the reactor. Catalytic pyrolysis can solve the above problems [20]. 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 achieve higher hydrogen production and lower tar yield [21, 22]. In the mixed gasification experiment of PE and wood chips, the yield of syngas, H₂ and hydrocarbons all reached the highest value when the percentage of the PE is about 80wt% [21]. 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 processes [22]. Lopez et al. [23] 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, and 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 stability [24]. Guo et al. [25] 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 [26–29]. Five Ni/C catalysts with different Ni content were tested [30], the sample containing 13.2wt% Ni showed the highest CH₄ conversion rate in the methane dry reforming experiment at 800 °C, and the H₂ concentration was 31.4 vol%. After 6 h of operation, the catalyst activity is still 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 had been studied by Chai et al. [31, 32]. With the addition of 30wt%-40wt% plastic, the H₂ yield was obtained by 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 and can provide sufficient surface area, is an ideal catalyst support. The cost of using activated carbon may be very high. According to statistics [33, 34], the annual throughput of bamboo charcoal in China can reach 40,000 tons, but the use of bamboo charcoal is still insufficient. Bamboo charcoal has the same adsorption capacity as activated carbon, and its porosity is about 5 times that of charcoal [35]. The excellent performance of bamboo charcoal has also been recognized by many researchers. Bamboo charcoal has developed pore structure, strong mechanical strength and good thermal stability, which makes it widely used as biomass adsorbent, catalyst support, and so on [36–38]. Studies [39] have shown that even if the bamboo charcoal is carbonized at 1000 °C, it will still retain porous nature of the original bamboo. When bamboo charcoal is used as a support, surface particles will stay in the pores, which overcome the shortcomings of other catalysts that are easy to aggregate [40].

Nickel-based catalysts have been widely used in pyrolysis due to their excellent tar cracking and reforming properties [18, 41, 42]. Unfortunately, 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 successfully reported by Santamaria et al. [43]. 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 the gasification of coke precursors. The CeO₂ structure has highly movable vacancy oxygen sites, reducing the degree of carbon deposition. What is more, reports [44–46] show that the addition of precious metals such as Ce, La, and Co [47] can reduce the degree of coking of Ni-based catalysts and improve the dispersibility of active metals. Zhang et al. [48] 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 h of operation. Ce or La was introduced to prepare a modified Cu-SAPO-34 catalyst [49]. 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.

The above information has been considered, so the focus of this work is to develop an efficient catalyst for co-pyrolysis of straw and PE to achieve higher H₂ production. Composite support ACB (Al₂O₃-CeO₂-bamboo charcoal) was synthesized by co-precipitation. Ni/ACB and Ni-La/ACB catalysts were synthesized based on it. The effects of straw/PE ratio, the presence and stability of catalyst on the H₂ 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 h to eliminate the influence of moisture in the pyrolysis experiment. PE powder purchased is 40 mesh, and it is also dried for 24 h 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 support, 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.

### 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 (Al2O3-CeO2-bamboo charcoal) was prepared by co-precipitation method. A certain amount of Al(NO3)3·9H2O, Ce(NO3)2·4H2O, 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 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 3 h to obtain ACB. The molar ratio of each component in the composite support is 1:1:1.

Ni(NO3)2·6H2O 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, Ni(NO3)2·6H2O, and CO(NH2)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 500-ml round bottom flask. The blend was reacted in an oil bath at 115 °C for 2 h, resulting in the precursor deposited on the support. After the reaction was complete, the mixture was filtered and washed until it became neutral, and then dried overnight. Finally, the product dried was calcined in a nitrogen atmosphere at 750 °C for 2 h 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, La(NO3)3·6H2O 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.

First, place the two quartz boats filled with catalyst and pyrolysis materials in the pyrolysis furnace respectively, and place furnace plugs on the left and right sides to ensure that the gas after the pyrolysis of the materials can fully contact with catalyst. Then close the flanges on both sides. Next, nitrogen is used to purge the air in the furnace for 20 min 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 to eliminate the influence of tar and enters the gas analyzer after being dried to determine the gas composition and content, and record the experimental data. Each group of tests was repeated three times to take the average value to ensure the reliability of the collected data.

### Table 1 Proximate and ultimate analysis of Soybean straw and PE

| Materials        | Ultimate analysis (wt%) | Proximate analysis (wt%) |
|------------------|-------------------------|--------------------------|
|                  | C          | H          | O*         | N         | S         | M_d | A_d | V_d | FC_d |
| 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 | –     |

*C calculated by difference; ad on air dried basis, d on dry basis*
Analytical Methods

The thermogravimetric (TG) analysis of the pyrolysis raw material and support is completed in the thermal analysis instrument (SDT Q600, TA). During the whole analysis process, the samples were heated to 850 °C at a heating rate of 20 °C/min under a nitrogen atmosphere. The specific surface area, pore volume and pore diameter of the support and catalysts were measured by the internal program of the specific surface area and porosity analyzer (ASAP 2460, Micromeritics) under N₂ atmosphere at 77.2 K. The pore structure characteristics of the samples were analyzed by N₂ adsorption and desorption isotherm, and the pore size distribution of the samples were obtained from the desorption branch by the BJH method. The material composition of the support and catalysts were measured by X-ray fluorescence spectrometry (EDX-7200, Shimadzu) and X-ray diffraction (XRD-600, Shimadzu). For XRF analysis, the catalyst was weighed 2 g after thorough drying and placed in the sample chamber for automatic quantitative analysis at room temperature and humidity < 70%. Finally, the weight percentage of each element (in oxide form) was obtained. For XRD analysis, using Cu-Kα radiation source, the scanning range was 10°–90°, the scanning speed was 6°/min, and the XRD patterns were obtained under the conditions of tube voltage 40.0 kV and current 30.0 mA. The surface microstructure of the catalysts and the used catalysts were observed by scanning electron microscope combined with EDX and EDS. First, the sample was dipped and glued to the sample stage with conductive glue. Then, use the washing ear ball to blow off the excess sample and spray gold. Adjust the acceleration voltage to 20.0 kV. The SEM images were obtained on scanning electron microscope (JSM-7100F, JEOL). The Gasboard analyzer (Gasboard-3100) was used to analyze the gas composition at room temperature. It can measure the volume concentration of CO, CO₂, CH₄, H₂, and other gases at the same time, and automatically calculate the calorific value of the gas. Then the hydrogen production rate was calculated based on gas composition.

Results and Discussion

TG Analysis of Materials

Figure 2 shows the TG and DTG curves obtained from the pyrolysis of soybean straw, PE, soybean straw, and PE. In the TG analysis of soybean straw and PE, the two were mixed at a mass ratio of 1:1. 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 [50]; 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 [51]. 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 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 [51]. 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.

TG Analysis of Support

Figure 3 is the thermogravimetric curve diagram of the support. TG analysis for support is to determine
the thermal stability. 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. From that, the support no longer continues to lose weight, and the overall weight loss rate is less than 10wt%. Indicating that the thermal stability of it is good and can provide more stable support for the catalyst.

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

Fig. 3 TG analysis of support
BET Analysis and Pore Size Distribution

The morphological characteristics of support ACB, catalysts Ni/ACB, and Ni-La/ACB were characterized by BET analysis. The results of their specific surface area, pore volume, and average pore diameter are shown in Table 2. The pore size distribution diagram and N$_2$-adsorption/desorption curve of the support and catalysts are shown in Fig. 4.

From the results in Table 2, it can be concluded that the specific surface area of the support and the catalysts are all high. A catalyst with a high specific surface area can fully contact with the reactants, and a support with a high specific surface area can reduce the aggregation of its surface-active components as much as possible [52, 53]. Similarly, it also can be seen from the table that the specific surface area of the catalysts is lower than that of the support, but this reduction is not serious, which can be explained by the reduction in specific surface area caused by the loading of active components [54, 55]. However, the loading of active components also makes the pore volume and pore diameter of the catalysts gradually larger. Studies have shown that

| Sample       | BET surface area (m$^2$·g$^{-1}$) | Pore volume (m$^3$·g$^{-1}$) | Average pore diameter (nm) |
|--------------|-----------------------------------|------------------------------|-----------------------------|
| ACB          | 86.9116                           | 0.0953                       | 4.2667                      |
| Ni/ACB       | 81.3061                           | 0.1674                       | 7.1807                      |
| Ni-La/ACB    | 75.6022                           | 0.1533                       | 7.5229                      |

Fig. 4 N$_2$-adsorption/desorption isotherm and BJH pore size distribution of support and catalysts: a ACB, b Ni/ACB, c Ni-La/ACB
the increase in pore volume and pore diameter of the catalyst within a certain range indicates that its load capacity is relatively strong, and the catalytic performance has also been improved [56].

Figure 4 shows the pore size distribution diagram and N\textsubscript{2}-adsorption/desorption curve of ACB, Ni/ACB, and Ni-La/ACB, respectively. The pore size distribution diagram shows that the pore sizes of the support and the two catalysts are mainly distributed between 0 and 20 nm, indicating that the material is a mesoporous material. Mesoporous materials play an important role in the catalytic reaction. The uniformity of the pore diameters of the three is relatively high. After the active components were loaded, the peak position only moves slightly, so the catalysts are still good mesoporous materials. It can be seen from the N\textsubscript{2}-adsorption/desorption curve that the isotherms of ACB, Ni/ACB, and Ni-La/ACB all have obvious hysteresis loops. According to the classification of IUPAC, they all belong to type IV adsorption isotherms. The type IV isotherm is derived from mesoporous materials, which is consistent with the analysis results of the pore size distribution diagram. The hysteresis loop of the support conforms to the H2 type, while the hysteresis loops of the catalysts belong to the H3 type. It can be inferred that the pore structure of the catalysts is changed after the active component is loaded.

**XRF Analysis**

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\textsubscript{2}O\textsubscript{3} and CeO\textsubscript{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\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{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.

**SEM Analysis of Catalysts**

As shown in Fig. 6, the apparent morphology of catalysts is observed by SEM. Figure 6a shows that the Ni/ACB presents a staggering flake structure, Ni is uniformly dispersed on the flake layer. After adding the auxiliary La, as shown in Fig. 6b, 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 [60]. The EDX spectrum on the right is an analysis of the substances in the catalyst. Numerous 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 support. These characterization results confirm the above characterization results again. Figure 6c, d shows SEM images of the used catalysts. It can be seen from the figure that there are a lot of filamentous carbon deposits on the surface of the used catalysts, and the surface morphology of the catalysts have undergone a relatively large change, and even some agglomeration phenomena have occurred. However, the overall dispersion of the elements on the catalysts surface is relatively high. Comparing the two, it is found that on the surface of the used Ni/ACB catalyst, the Ni element is basically in a uniformly dispersed state, but its uniformity is not as well as that of the used Ni-La/ACB catalyst. Similarly, the overall dispersion of La element on the surface of the used Ni-La/ACB catalyst is better.

**Co-pyrolysis Experiment**

**Influence of Straw/PE Ratio**

The effect of mass ratio of straw and PE on the yield and composition of pyrolysis gas have been explored, and the straw/PE ratio was varied from 10:0 to 0:10. The
pyrolysis experiment was carried out without catalyst and the pyrolysis temperature was 700 °C. The results are shown in Fig. 7. In the experiment to explore the influence of the ratio of Straw/PE, the experimental error is between 1.4% and 5.03%. With the increase of PE, the output of \( \text{H}_2 \) showed a trend of first increasing and then decreasing. When the mass ratio of straw/PE was 5:5, the highest \( \text{H}_2 \) yield is 2.81 mmol/g. As observed, increasing the proportion of PE in the raw material will cause changes in the gas composition, especially \( \text{CO} \) and \( \text{CO}_2 \) are significantly reduced due to the decrease in the O content in the raw materials. The total gas production shows a trend of first increasing, then decreasing and then increasing, which is related to the increase of \( \text{CH}_4 \) yield and the decrease of \( \text{CO} \) and \( \text{CO}_2 \) yield after PE is added. Plastic is the main source of \( \text{H}_2 \) and \( \text{CH}_4 \), and increasing its proportion can significantly increase the output of \( \text{H}_2 \) and \( \text{CH}_4 \). 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 pine sawdust and HDPE was reported [61]. Biomass/plastic ratio of 0.5 was found for a catalyst to play the best roles in the \( \text{H}_2 \)-rich syngas quality. In the following experiments, the mass ratio of straw/PE is 5:5.

**Influence of Catalyst**

Figure 8 shows the effect of different catalysts on straw and PE co-pyrolysis. In the experimental process of verifying the influence of the catalyst on the gas production, the experimental error value is between 1.1 and 3.3%. Biomass pyrolysis will produce tar and gas without catalyst. As shown in Fig. 8, the \( \text{H}_2 \) concentration is only 20.65 vol% without catalyst, while the \( \text{CH}_4 \) concentration rises to 51.12 vol%. The \( \text{H}_2 \) concentration upgrades significantly in the presence of catalysts, and it can reach up to 56.4 vol%. Catalysts participate in the following reactions (Eqs. (1)–(7)) [8]. 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 \( \text{H}_2 \) and \( \text{CO} \) to obtain more high-value gases.

\[
\begin{align*}
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{H}_2 \quad (1) \\
\text{C} + \text{H}_2\text{O} & \rightarrow \text{H}_2 + \text{CO} \quad (2) \\
\text{C} + 2\text{H}_2\text{O} & \rightarrow \text{CH}_4 + \text{CO}_2 \quad (3) \\
\text{CO} + 3\text{H}_2 & \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad (4)
\end{align*}
\]
**Fig. 6** SEM images of catalysts: a Ni/ACB, b Ni-La/ACB, c used Ni/ACB, d used Ni-La/ACB

**Fig. 7** Gas production when changing straw/PE ratio (temperature 700 °C)
In co-pyrolysis experiments, the content of H₂ has increased intensely, CO content increased slightly, CH₄ and CO₂ content have marked decreased in the presence of catalysts. According to Eq. (6), in the dry reforming reaction of tar, hydrocarbons combine with CO₂ are converted into H₂ and CO. The H₂ yields are 12.56 mmol/g(Ni/ACB) and 13.56 mmol/g(Ni-La/ACB), respectively, which are much higher than the hydrogen yield without catalyst (2.81 mmol/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.

### 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. 9. The error values of the whole experiment were within 3%.

\[
\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \tag{5}
\]

\[
\text{C}_n\text{H}_m + n\text{CO}_2 \rightarrow (m/2)\text{H}_2 + 2n\text{CO} \tag{6}
\]

\[
\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2 \tag{7}
\]

In co-pyrolysis experiments, the content of H₂ has increased intensely, CO content have increased slightly, CH₄ and CO₂ content have marked decreased in the presence of catalysts. According to Eq. (6), in the dry reforming reaction of tar, hydrocarbons combine with CO₂ are converted into H₂ and CO. The H₂ yields are 12.56 mmol/g(Ni/ACB) and 13.56 mmol/g(Ni-La/ACB), respectively, which are much higher than the hydrogen yield without catalyst (2.81 mmol/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.

Figure 9a shows the hydrogen production of straw pyrolysis, and Fig. 9b 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 [62]. Comparing Fig. 9a and b once again proves that adding plastic can increase the concentration of H₂.

Figure 9b 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 [63] that the products of polyolefin pyrolysis are mainly long-chain alkanes and olefins. Barbarias et al. [64] 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. 9b, 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.
Combined with the SEM image of used Ni-La/ACB catalyst. It can be concluded that the distribution basis of La element is relatively uniform after six experiments, so the catalyst that can still maintain high activity. 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 the chart in Fig. 9a, in co-pyrolysis experiment, the H$_2$ concentration was 30.8 vol% (Ni/ACB) and 43.52 vol% (Ni-La/ACB) after 6 experiments, respectively.

**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 H$_2$ yield 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. It is concluded through experiments that adding an appropriate amount of PE is beneficial to increase the output of H$_2$ when the straw and plastic are co-heated to produce hydrogen. With the increase of the proportion of plastic in the pyrolysis, the H$_2$ yield will increase firstly and then decrease. When the straw/PE ratio is 5:5, the maximum H$_2$ yield is 2.81 mmol/g;

2. The presence of the catalyst has played a significant role in promoting the production of hydrogen in co-pyrolysis. The H$_2$ yield were 12.56 mmol/g (Ni/ACB) and 13.56 mmol/g (Ni-La/ACB). Indicating that the Ni-La/ACB has the best catalytic performance and can effectively increase the yield of H$_2$.

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 addition of La also slowed down the deposition of carbon on the surface of the catalysts. The stability of Ni-La/ACB in the co-pyrolysis experiment was the best. After 6 experiments, the H$_2$ concentration was only reduced from the initial 56.4 vol% to 43.52 vol%.

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**Declarations**

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

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

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