ABSTRACT: A two-stage pyrolysis fixed bed was used, and the vapor-modified pyrolysis coke was used as a carrier. A ZHPC catalyst was prepared by plasma calcination. Gas-phase tar produced by the pyrolysis of raw coal was subjected to in situ catalytic cracking to improve tar and gas yield. The effects of plasma calcination power, calcination time, and ZnO loading on in situ cracked products were studied. The prepared catalyst was characterized by X-ray electron spectroscopy, X-ray diffraction, Brunauer–Emmett–Teller, and scanning electron microscopy. The results showed that (1) compared with traditional catalysts, the catalyst prepared by plasma has better performance; (2) the optimal calcination time of the ZHPC catalyst is 5 min, calcination power is 60 W, and ZnO loading is 10%; (3) compared with raw coal pyrolysis, the optimal ZHPC catalyst on in situ catalytic cracking tar, gas yield increased by 66.16%; the cracking rate of tar increased by 54.46%, and the content of light components increased to 60.7%; (4) in situ catalytic cracking of tar with the optimal PC, the light tar has been greatly improved, in which the light oil, phenol oil, naphthalene oil, and wash oil have increased by 93.04, 126.31, 257.28, and 108.08%, respectively. The anthracene oil and asphalt have decreased by 26.98 and 58.71%; the tar cracking rate has increased.

1. INTRODUCTION

With the development of coal utilization technologies such as gasification, liquefaction, carbonization, and coking, a large number of coal tar or coal tar by-products have been produced, among which carbonization and liquefaction are the processes with coal tar as the main product.1–3 Although medium and low-temperature coal tar has higher contents of aliphatic hydrocarbons and light aromatics than high-temperature coal tar, they can be used as raw materials for liquid fuels and chemicals, and the content of heavy components in coal tar produced by the existing medium and low-temperature pyrolysis process is still as high as about 50%.3–5 With the development of economy and the urgency of environmental protection, the quality requirements for fuel oil are becoming higher and higher, so the use of coal tar to produce cleaner liquid fuels has become a research hotspot.6

The middle and low-temperature coal tar produced by carbonization has not been cracked secondarily. Therefore, there are many light components in the medium and low-temperature coal tar.7 The light fractions obtained after fractionation can be used for blending gasoline and diesel. High temperature cracking is the process of converting large molecules into small molecular compounds, but it requires high equipment, more energy consumption, and easily blocks pipelines.8–10 Through hydrocracking, coal tar can obtain gasoline, diesel oil, kerosene, and other distillate fuels. Catalytic cracking can overcome the shortcomings of thermal cracking, reduce the activation energy of molecular reactions, and thus reduce the reaction temperature.11

Compared with the traditional coal tar hydrogenation process, the coal pyrolysis and tar catalytic cracking processes are performed simultaneously, the energy consumption is lower, and it has better economic benefits.12–14 Meanwhile, the heavy components are degraded to form small molecular substances, which are more conducive to the condensation and separation of coal tar downstream of the process.15 The in situ catalytic cracking of gas tar is that the gas tar from coal pyrolysis enters into the catalytic layer for catalytic cracking before it is condensed. Under the action of catalyst and heat, the heavy components in coal tar undergo cracking and aromatization reactions and are converted into light aromatics, oil products, gases, and so forth.16–18 The advantage of gas-phase tar in situ catalytic cracking is that the heavy components in tar are lightened, which can increase their utilization value. The lighting of tar can solve the problem of equipment and pipeline blockage caused by the condensation of heavy components in tar.19,20 The catalyst is also easily separated

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and recovered in the catalytic layer. High-temperature gas-phase tar produced by pyrolysis enters the catalytic layer for catalysis, which avoids the energy consumption of tar heating in the traditional catalytic cracking process and improves the energy efficiency of the process.21–23

In the process of in situ catalytic cracking to achieve gas tar upgrading, the choice of catalyst is particularly important. Metal oxide catalysts show good hydrogenation performance during coal pyrolysis and can reduce the hydrogenation reaction temperature, which is very suitable as a catalyst for coal pyrolysis to produce tar.24 The molecular sieve catalyst has the advantages of a unique pore structure, large specific surface area, strong acidity, and good selective catalytic performance.25,26 It can convert the aromatic compounds in the thick ring during pyrolysis into useful chemicals and raw materials in the chemical industry. The supported catalyst can flexibly control its physical and chemical properties and improve its catalytic performance through the choice of support, active components, auxiliaries, and changes in preparation process conditions.27–29 Therefore, it has been widely studied in the catalytic cracking of coal tar. In recent years, coal-based carbon materials have also been widely used, such as activated carbon, foamed carbon, pyrolytic coke, and carbon-based supported catalysts.30

In order to improve the ratio of light oil, the active component loaded on pyrolysis coke is considered in this paper, which leads to the problem of the preparation method of the supported catalyst.31 The traditional catalyst preparation method generally adopts the impregnation or sol–gel method.32 Both methods must adopt the calcination method. The calcination temperature is above 300 °C.33 This high-temperature calcination process will cause pyrolysis coke to ignite. The process must be completed in an anaerobic environment. Therefore, it is difficult to control the process, and even if the reaction conditions are controlled, the prepared catalyst is prone to agglomeration, the active component distribution of the catalyst is uneven, and the catalytic activity is low. Based on the above problems, a low-temperature plasma calcination method is proposed to prepare a pyrolysis coke-supported catalyst. Low-temperature plasma, as an effective technical method, has become increasingly connected with the catalyst field. Compared with traditional catalysts, the catalyst has many significant advantages such as short preparation time, large specific surface area of the catalyst, high dispersion of active components, many lattice defects, and good stability, which can fully meet the above requirements.34,35

In this paper, a vapor-modified pyrolysis coke was used as the carrier, the ZHPC catalyst was prepared by plasma calcination, and the catalyst was subjected to heavy tar cracking and characterized by Brunauer–Emmett–Teller (BET), X-ray electron spectroscopy (XPS), X-ray diffraction (XRD), and scanning electron microscopy (SEM). It can achieve comprehensive utilization of coal and improves tar yield.

2. RESULTS AND DISCUSSION

2.1. Coal Sample Analysis. 2.1.1. Proximate and Ultimate Analyses. Table 1 shows the proximate and ultimate analyses of coal samples.

| Sample       | Mdaf (wt %) | Aad (wt %) | Vad (wt %) | FCad (wt %) | C (wt %) | H (wt %) | N (wt %) |
|--------------|-------------|------------|------------|-------------|----------|----------|----------|
| coal sample  | proximate analysis/% | ultimate analysis/% |
|              | Mda | Aa | Va | FCa | C   | H   | N   |
| 15.23        | 16.58 | 36.56 | 32.53 | 58.93 | 4.093 | 1.136 |

Table 1. Proximate and Ultimate Analyses of Coal Samples (%)

2.1.2. Thermal Weight Analysis of Lignite. The weight loss curve [thermogravimetric (TG) analysis] and the weight loss rate curve [derivative thermogravimetric (DTG) analysis] of lignite under a N2 atmosphere at a heating rate of 15 °C/min are shown in Figure 1. It can be seen that the weight loss of lignite was divided into three stages. The first stage was between room temperature and 150 °C, called the drying stage, mainly the precipitation of moisture and adsorbed gas. The second stage was between 150 and 300 °C; this stage was in the preheating stage. No obvious pyrolysis occurred. There was no obvious change in the TG and DTG curves. The third stage was between 300 and 500 °C. This stage was a pyrolysis stage of coal, where functional groups were decomposed such as a phenolic carboxyl group having a poor thermal stability in a molecular structure and a bridge structure was broken between an aromatic ring and a side chain of a fat in a macromolecular network. A large number of gaseous hydrocarbons and tar vapors were released. The coal lost weight quickly and had a maximum rate of weight loss. The DT curve of the coal dropped sharply after 400 °C, and the DTG curve also showed the highest peak of weight loss. The peak temperature of the pyrolysis was 450 °C, which was the temperature corresponding to the maximum weight loss temperature. The maximum weight loss temperature reflected the stability of the coal macromolecular structure. The lower the peak temperature, the more easily the network structure in coal was destroyed. The higher the reactivity of coal, the more unstable the structure was during pyrolysis.

2.2. Effect of the ZHPC Catalyst on Tar Cracking under Different Plasma Calcination Conditions. 2.2.1. Effect of the ZHPC Catalyst on Tar Cracking under Different Plasma Calcination Time. The optimal vapor-modified pyrolysis coke (HPC) was prepared by an equal volume impregnation method with a supported 5% loading pyrolysis catalyst; it was placed in a plasma reactor and calcined in an oxygen atmosphere. The calcination power was 45 W, and the calcination time was 1, 3, 5, and 8 min to prepare ZHPC catalysts, namely, ZHPC-1min, ZHPC-3min, ZHPC-5min, and ZHPC-8min, respectively; 3 g was weighed for tar cracking. Figure 2 is the effect of ZHPC on tar cracking by plasma at different calcination times.

As can be seen from Figure 2a, after the plasma calcination of ZHPC as a catalyst, with the increase of the plasma calcination time, the total yield of pyrolysis gas first increases and then decreases, and the tar first decreases and then increases. Among them, under the condition of ZHPC-5min, the tar produced by pyrolysis coke cracking is at least 0.63632 g. The yield of catalytic cracking tar is reduced by 0.688 g, and the tar cracking efficiency is improved by 51.9%. The pyrolysis coke catalytic cracking produced the largest amount of gas; the total gas yield
Temperature bridges such as ff be cracked when they undergo di compounds and complex components. Many substances will oxygen, nitrogen, and sulfur. There are many types of aromatic hydrocarbons, and heterocyclic compounds containing large number of chain hydrocarbons, cyclic hydrocarbons, calcination times have di decreasing, indicating ZHPC of plasma with di produced by cracking tar show a trend of increasing and then H2, CH4, and CO produced by catalytic pyrolysis of ZHPC-cracking e calcination times of the plasma, the order of the pyrolysis component proportion of tar.

Therefore, from the perspective of tar composition changes, highest, and the anthracene oil and asphalt are reduced the most. ZHPC-5min tar cracking is obvious, the overall contents of light oil, phenol oil, naphthalene oil and washing oil produced are the ZHPC-5min tar cracking is obvious, and the proportion of light group is higher, and the effect is better. ZHPC-5min tar cracking is obvious, and the proportion of light components increased from 36.65 to 55.80%.

Figure 2b shows that after ZHPC of plasma with different calcination times, the amounts of H2, CO2, CH4 and CO gases produced by cracking tar show a trend of increasing and then decreasing, indicating ZHPC of plasma with different calcination times have different effects. The combustible gas H2, CH4 and CO produced by catalytic pyrolysis of ZHPC-5min increased to a large extent compared with the pyrolysis of raw coal. Because the more combustible the gas produced by pyrolysis coke catalytic cracking of gas tar, the better the effect of ZHPC-5min on gas tar cracking.

Figure 2c shows the effect of ZHPC on tar composition at different calcination times. In the tar grouping, the higher the calcination time, the order of the pyrolysis coke rises, and fewer active sites are generated. With the increase of modification time, the number of high energy oxygen containing particles ionized from the system increases, the etching strength of organic matter on the catalyst surface increases, and the metal salt ions loaded on the catalyst surface have enough time for oxidation reaction to generate oxides conducive to tar cracking. The number of active sites on the catalyst surface also gradually increases, which significantly improved the chemical properties of the catalyst surface, thus increasing tar cracking efficiency and gas production. However, the modification time should not be too long. Such a large number of high energy particles will destroy the pore structure of the catalyst, change the position of the original effective active site, and reduce the effect of the catalyst. Therefore, the effect of ZHPC-5min on gas tar cracking is better.

2.2.2. Effect of the ZHPC Catalyst on Tar Cracking under Different Plasma Calcination Powers. The optimal HPC was prepared by a volumetric immersion method with a supported 5% loading pyrolysis catalyst. The catalyst was placed in a plasma reactor and calcined in an oxygen atmosphere, and the calcination power was 45, 60, and 75 W, respectively. Calcination time was 5 min to prepare the ZHPC catalyst,

Table 2. Changes of Light and Heavy Components after Tar Cracking

|                  | coal | PC   | HPC  | ZHPC-1min | ZHPC-3min | ZHPC-5min | ZHPC-8min |
|------------------|------|------|------|-----------|-----------|-----------|-----------|
| light component (g) |      |      |      | 0.3551    | 0.4390    | 0.4537    | 0.3698    |
| heavy component (g) |      |      |      | 0.9689    | 0.7620    | 0.5512    | 0.3279    |
| light component ratio (%) |      |      |      | 26.8      | 36.55     | 45.15     | 53        |

CH2 + H2O → CO + 2H2

(1)

CH2 + O → CO + 2H2

(2)

Figure 2 shows that the effect of ZHPC-5min on gas tar cracking is better and the proportion of light components is the highest. Because of the short effective discharge time of the plasma, fewer active particles are generated, the zinc nitrate loaded on the pyrolytic coke surface cannot be fully oxidized by the plasma, and fewer active sites are generated. With the increase of modification time, the number of high energy oxygen containing particles ionized from the system increases, the etching strength of organic matter on the catalyst surface increases, and the metal salt ions loaded on the catalyst surface have enough time for oxidation reaction to generate oxides conducive to tar cracking. The number of active sites on the catalyst surface also gradually increases, which significantly improved the chemical properties of the catalyst surface, thus increasing tar cracking efficiency and gas production. However, the modification time should not be too long. Such a large number of high energy particles will destroy the pore structure of the catalyst, change the position of the original effective active site, and reduce the effect of the catalyst. Therefore, the effect of ZHPC-5min on gas tar cracking is better.

![Graphs and charts showing the effects of plasma calcination times on tar cracking](image-url)
namely, ZHPC-45W, ZHPC-60W, and ZHPC-75W, 3 g was weighed for tar cracking. Figure 3 is the effect of the ZHPC catalyst on tar cracking under different plasma calcination powers.

It can be seen from Figure 3a that with the increase of plasma calcination power, the total yield of pyrolysis gas increases first and then decreases, and the tar decreases first and then increases. Among them, under the condition of ZHPC-60W, the tar produced by pyrolysis coke catalytic cracking is at least 0.62277 g, and the tar is reduced by 0.701 g and increased by 52.9%. The pyrolysis coke catalytic cracking produced the largest amount of gas; the total gas yield reached 16.35 L and increased by 65.1%. Therefore, at different calcination power of the plasma, the order of pyrolysis cracking effect is 60 W > 45 W > 75 W.

It can be seen from Figure 3b that after ZHPC by plasma with different calcination power, with the increase of power, the amounts of H\(_2\), CO\(_2\), CH\(_4\) and CO gases produced by tar cracking will increase first and then decrease. This shows different calcination powers of plasma have different effects. Comparing ZHPC-45W and ZHPC-75W, the flammable gases H\(_2\), CH\(_4\), and CO produced by the ZHPC-60W catalytic cracking have increased to a greater extent. The more flammable the gas produced by pyrolytic coking catalytic cracking of gas-phase tar, the better. Therefore, the plasma calcination power is 60 W, and the pyrolysis coke has the best cracking effect.

Figure 3c shows the effect of ZHPC with different calcination powers on tar composition. It can be seen that when pyrolysis coke with different calcination powers of the plasma is added, tars with different boiling points are cracked to make the percentage content change. ZHPC-60W tar oil crack obviously, which caused the asphalt content to be greatly reduced, and the content of anthracene oil is increased; the contents of light oil and phenol oil are significantly increased; naphthalene oil and washing oil produced by tar oil are reduced. Therefore, from the perspective of tar composition changes, ZHPC-60W tar has the best cracking effect.

Table 3 shows the changes of light and heavy components after tar cracking.

| calcination power | coal | PC | HPC | ZHPC-45W | ZHPC-60W | ZHPC-75W |
|-------------------|------|----|-----|---------|---------|---------|
| light component (g) | 0.3551 | 0.4390 | 0.4537 | 0.3551 | 0.3693 | 0.3740 |
| heavy component (g) | 0.9689 | 0.7620 | 0.5512 | 0.2813 | 0.2535 | 0.3123 |
| light component ratio (%) | 26.8 | 36.55 | 45.15 | 57.01 | 59.30 | 54.50 |

Figure 4. Effect of ZHPC on tar cracking under different ZnO loadings. (a) Total gas and tar yield. (b) Gas yield. (c) Component proportion of tar.
faster high energy oxygen containing particles in the system, the
etching effect on the catalyst surface is not obvious, and the
modification effect is poor. When the modification power is 75
W, the plasma discharge is violent. During the modification
process, the high energy oxygen containing electron flow
constantly strikes the catalyst surface, destroys the original
functional group structure and pore structure, and deactivates
the active site, resulting in the decrease of the effect. When the
modified power is 60 W, the tar cracking efficiency and gas
production are the highest, and the proportion of flammable gas
is higher than other powers. This is because the zinc nitrate on
the pyrolytic coke surface is completely converted into zinc
oxide and uniformly distributed on the catalyst surface, resulting
in an increase in active sites and the best effect of tar cracking.
Therefore, the optimal modification power is 60 W.

2.2.3. Effect of Pyrolytic Coke on Tar Cracking under
Different ZnO Loadings. The optimal vapor-modified pyrolysis
coke was prepared by an equal volume impregnation method
with 5, 10, and 15% loading capacity of a supported pyrolysis
coke catalyst. The catalyst was placed in a plasma reactor, and
oxygen was introduced for calcination. The calcination power
was 60 W, and the calcination time was 5 min respectively.
ZHPC catalysts were prepared, namely, ZHPC-5%, ZHPC-10%,
and ZHPC-15%, and 3 g was weighed for tar cracking. Figure 4 is
the effect of ZHPC on tar cracking under different ZnO loadings.

Figure 4a shows the effect of ZHPC with different loading
amounts of ZnO on gas and tar yield. It can be seen that with
the increase of ZnO loading, the total yield of pyrolysis gas first
increases and then decreases and the tar decreases and then
increases. Under the condition of ZHPC-10%, the tar produces
at least 0.60277 g, the yield of catalytic cracking tar is reduced by
0.721 g and increased by 54.47%. The pyrolysis coke catalytic
cracking produced the largest amount of gas, with a total gas
yield of 16.45 L, and increased by 66.16%. Therefore, the
cracking effect of ZHPC-10% is better.

Figure 4b shows the effect of ZHPC under different ZnO
loadings on the gas composition. It can be seen that the yields of
H₂, CO₂, CH₄, and CO produced by tar cracking change with
the addition of different loading amounts of ZnO, indicating that
it has different cracking effects. Compared with the raw coal, the
flammable gas (H₂, CH₄, and CO) produced after ZHPC-10%
 cracking has increased to a large extent. The more combustible
gas produced by ZHPC is, the better it is in situ catalytic cracking
of gas-phase tar. Therefore, the effect of ZHPC-10% tar cracking
to produce flammable gas is better.

Figure 4c shows the effect of different loading amounts of
ZnO on tar composition. It can be seen that ZHPC-10% has an
obvious tar cracking effect, which greatly reduces the asphalt
content, increases the anthracene oil content, obviously increases
the light oil and phenol oil contents, and slightly reduces the naphthalene oil content and wax oil content produced by tar cracking. Therefore, from the perspective of tar
composition changes, ZHPC-10% tar has the best cracking
effect. Figure 5a–c shows catalysts with a plasma calcination
time of 5 min, power of 60 W, and a ZnO loading of 10%. It can
be seen that because of the tar cracking, the light components of
the tar increase and the tar yield is improved.

Table 4 shows the changes of light components and heavy
components after ZHPC tar cracking. As can be seen, the proportion of light components in the tar is higher and the effect
is better. ZHPC-10min tar cracking is obvious.

It can be seen from Figure 4 that when ZnO loading is 10%,
the total amount of pyrolysis gas is the largest and the proportion
of combustible gas is also the highest. The reason may be that
when the loading is 10%, manganese nitrate attached to the
surface of pyrolysis coke is fully oxidized and the generated
manganese oxide can oxidize gaseous hydrocarbon to generate
hydrogen. When the loadings are 5 and 15%, because the plasma
treatment time is relatively short, the manganese nitrate
supported on the catalyst surface cannot be completely oxidized.
Hence, the catalytic effect is relatively poor and the optimal ZnO
loading can be determined to be 10%.

2.3. Catalyst Characterization. 2.3.1. BET of the Catalyst.
Before and after the reaction, the specific surface areas of
different catalysts are shown in Table 5. As can be seen, the
optimal vapor pyrolysis modification conditions make the
specific surface area the largest. After ZnO loading, the specific
surface area of pyrolysis coke becomes smaller, and the specific
surface area decreases as the load increases. The thermal
pyrolysis of the load forms ZnO particles inside it, which blocks
the thermally decomposed pores, and the more the load, the
more the oxide particles are formed and the larger the pores are
blocked. As it increases, the specific surface area of pyrolysis
becomes smaller. At the same time, after the reaction, the
specific surface area has also decreased to a large extent. The
main reason is that a portion of the tar molecules are adsorbed
on the surface, clogging the pores and reducing the specific
surface area. After the reaction, the specific surface area of
ZHPC-10% is similar to that of the optimal HPC.

2.3.2. XRD Pattern of the ZHPC Catalyst. Figure 6 shows the
XRD of the catalyst with different ZnO loadings. It can be seen
that after Zn-loaded pyrolysis coke modified by plasma
calcination, two kinds of metal oxides are formed on the
catalyst, namely, ZnO and ZnO₂, and the dispersion of the metal
oxide is relatively uniform. It can be seen that the plasma can
increase the dispersibility of the metal oxide. ZnO has better
crystallinity and dispersibility, while ZnO₂ has poor stability, can
form ZnO₂ → ZnO + 1/2O₂, so the amount of ZnO₂ formed on
the catalyst is very small. It is mainly ZnO that played a catalytic
role in the actual catalytic cracking reaction.

Although flammable gas (H₂, CH₄, and CO) is produced in
the pyrolysis process, the reducibility of Zn is stronger than that
of hydrogen, so it is difficult to decompose zinc oxide. Only
when the temperature reaches 1975 °C can zinc oxide
decompose to produce zinc vapor and oxygen. Elemental
carbon can be used for the reduction of zinc in zinc oxide and
react at high temperature.

2.3.3. XPS Pattern of the ZHPC Catalyst. It can be seen from
the peak of oxygen in Figure 7c that there are two forms of
oxygen in the catalyst, where 531.8 eV and 533.6 eV belongs
to lattice oxygen and chemical adsorption oxygen, respectively, and
the lattice oxygen intensity is significantly higher than the
chemical adsorption oxygen intensity. After the reaction, the
lattice oxygen area is largely reduced; therefore, the amount of
lattice oxygen after the reaction is less. It can be seen from the
peak of oxygen in Figure 8c that the intensity of the lattice oxygen increases and the strength of the chemisorbed oxygen decreases after the reaction, indicating that the lattice oxygen participated in the reaction during the reaction. As can be seen from Figures 7b and 8b, there are two peaks of zinc on the catalyst surface, 1022 eV is Zn 2p3/2, 1045 eV is Zn 2p1/2, and the oxide is ZnO. The strength of ZnO decreases after the reaction, indicating that ZnO plays a major role in the reaction. It can be seen from the XRD spectrum that the catalyst includes more ZnO, and this result can be better verified by combining XPS. It indicates that a highly active metal oxide is formed on the surface of the plasma calcination catalyst, which is favorable for promoting the cracking of the gas phase tar by the catalyst. In the whole process of catalytic cracking, ZnO plays a major catalytic role. ZnO is a P-type semiconductor with considerable nonstoichiometric oxygen present. Because coal mainly produces gaseous hydrocarbons during the pyrolysis stage, the formation of hydrogen is mainly due to the oxidative dehydrogenation of gaseous hydrocarbons. The mechanism of oxidative dehydrogenation of gaseous hydrocarbons on ZnO can be inferred as follows: first, gaseous hydrocarbons react with lattice oxygen [O] in ZnO to form a −H to form a hydrocarbyl radical and then further desorb a −H to form lower-order hydrocarbons. Therefore, we speculate the reaction mechanisms of oxidative dehydrogenation of gaseous hydrocarbons on ZnO catalysts which are as follows.

\[
\begin{align*}
C_nH_{2n+2} + [O] & \rightarrow C_nH_{2n+1} + OH^- \quad (3) \\
C_nH_{2n+1} + [O] & \rightarrow C_nH_{2n} + OH^- \quad (4) \\
OH^- + OH^- & \rightarrow H_2 + 2[O] \quad (5)
\end{align*}
\]

2.3.4. SEM Pattern of ZHPC-10%. It can be seen from Figure 9 that after ZnO loading, there are more particles on the surface. It is speculated that these particles may be zinc oxide, which provided more active sites for the gas phase tar. After tar cracking, the particles of ZHPC catalysts change greatly, and the number of particles decrease. Therefore, many particles and active sites are consumed in the process of cracking tar, and the effect of cracking tar is achieved (Figure 10).

3. CONCLUSIONS

In this paper, vapor-modified pyrolysis coke was used as the raw material. The ZnO-loaded pyrolysis coke catalyst is prepared by the equal impregnation method. The pyrolysis coke is calcined by plasma. The effects of ZnO loading, calcination time, and calcination power on tar cracking were studied. The results showed that:

1. Compared with traditional catalysts, the catalyst prepared by plasma has the advantages of short preparation time, large specific surface area, high dispersion of active
components, many lattice defects, and good stability which can fully meet the above requirements.

(2) Vapor-modified pyrolysis coke is used as carrier; the ZHPC catalyst is prepared by the plasma calcination method, and the catalyst cracks the heavy tar. The cracking effect of heavy tar is improved, and it can achieve comprehensive utilization of coal and improves tar yield.

(3) The optimal plasma calcination time is 5 min, calcination power is 60 W, and ZnO loading is 10%. The tar cracking effect is the best.

(4) Compared with the pyrolysis of raw coal, the yield of gas produced is increased from 9.9 to 16.45 L, that is, increased by 66.16%; the tar is decreased from 1.324 to 0.603 g, and the cracking rate of tar is increased by 54.46%.

4. MATERIALS AND METHODS

4.1. Materials. The lignite used in the experiment was produced in Ordos. The lignite was crushed, and particles with 3–5 mm were screened. The screened lignite particles was put into a 60 °C drying oven for drying and then put into a dryer for standby. In the experiment, 3–5 mm lignite particles were used to prepare different types of pyrolysis coke catalysts.

4.2. Preparation of the ZHPC Catalyst by Plasma.

(1) Weigh 100 g lignite particles and put them into the pyrolysis furnace. The pyrolysis constant temperature time of the pyrolysis furnace was 2 h, and the final pyrolysis temperature was 750 °C. Pyrolysis coke was prepared as the carrier of subsequent modification and named PC.

(2) PC was used as the carrier, placed in a tubular furnace, modified by vapor, and set at a constant flow rate of 450 mL/min, a temperature of 650 °C, and a time of 60 min, and the prepared pyrolysis coke catalyst was named HPC.

(3) The mass of zinc nitrate hexahydrate required for the preparation of ZHPC catalysts with 5% loading was 0.551 g, which was placed in a distilled zinc nitrate solution. Then, 3 g HPC was placed in a zinc nitrate solution, impregnated 24 h with the equivalent volume impregnation method, and dried for 1 h at 110 °C. The calculation formula of zinc nitrate required is as follows

\[
m_{\text{Zn(NO}_3\text{)}_2\text{.6H}_2\text{O}} = \frac{m_{\text{HPC}} \times 5\%}{M_{\text{ZnO}}} \times M_{\text{Zn(NO}_3\text{)}_2\text{.6H}_2\text{O}}
\]

(4) The HPC impregnated in (3) was placed in the plasma, and oxygen was used as the calcination atmosphere. The flow rate was 60 mL/min, calcination power was 45 W, and calcination time was 1, 3, 5, and 8 min. ZHPC catalysts with different plasma calcination times were prepared and named ZHPC-1min, ZHPC-3min, ZHPC-5min, and ZHPC-8min, respectively.

(5) Taking the optimal time of plasma in (4) as the calcination time, the impregnated HPC was placed in the plasma, oxygen was used as the calcination atmosphere, the flow rate was 60 mL/min, and powers were 45, 60, and 75 W. ZHPC catalysts with different calcination powers were prepared, which were named ZHPC-45W, ZHPC-60W, and ZHPC-75W.

(6) Taking the optimal power of plasma in (5) as the optimal calcination power, the impregnated HPC with 5, 10, and 15% ZnO loadings were prepared by the equal volume impregnation method. The impregnated HPC was placed in the plasma, oxygen was used as the calcination atmosphere, the flow rate was set to 60 mL/min, and time was 5 min. ZHPC catalysts with different loadings were prepared by the plasma calcination, which were named ZHPC-5%, ZHPC-10%, and ZHPC-15%.

4.3. Catalyst Activity Evaluation. 4.4. Detection of the Gas and the Tar. 4.4.1. Gas Detection. The gas produced by catalytic cracking of tar gas is collected using the gas collecting bag. The gas composition was analyzed using an Agilent-7820A
Table 6. Boiling Point Ranges for Classifying Tar Fractions

| coal tar fraction | boiling point (°C) | light oil | phenolic oil | naphthalene oil | washing oil | anthracene oil | asphalt |
|-------------------|--------------------|-----------|--------------|----------------|-------------|----------------|--------|
|                   | <170               | 170–210   | 210–230      | 230–300        | 300–360     | >360           |

**Author Contributions**

Conceptualization, Zhang Lei(F) and Zhang Lei(M); methodology, S.H.; software, J.Y.; validation, J.Y.; investigation, Zhang Lei(M); data curation, K.W.; writing-original draft preparation, S.H.; and writing-review & editing, S.H.

**Notes**

The authors declare no competing financial interest.

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