Study on microwave pyrolysis of Mengdong lignite by Fe/Ca@Al₂O₃ catalyst

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Abstract: Microwave pyrolysis coal has the characteristics of fast heating, short time and high content of active components. In order to further improve the production and relative content of hydrogen(H₂) and carbon monoxide(CO) during microwave pyrolysis of lignite, Fe/Ca@Al₂O₃ catalyst was synthesized by co-precipitation with Al₂O₃ as the carrier, and the effect of Fe/Ca ratio on the production and content of active components (CO+H₂) in pyrolysis gas was studied. With the addition of catalysts, the pyrolysis process was advanced, and the final temperature rise was high. 12Ca/Fe catalyst has the most obvious effect on improving the production of H₂ and CO, with an increase rate of 36.6% and 54.8%, respectively.

1. Introduction
Microwave pyrolysis coal has the characteristics of fast heating, short time and high content of active components. However, lignite has poor microwave absorption ability. By adding semi-coke and other wave-absorbing materials, the heating state of lignite can be improved and the pyrolysis efficiency can be further improved[1,2]. The study[3,4] shows that the salt or oxide of Fe, Ca and other metal elements in the ash content of lignite can improve the production and quality of pyrolysis gas, among which Fe has an obvious catalytic effect on the formation of H₂. Therefore, it is very important to study the basic characteristics of microwave pyrolysis of lignite and its gas production.

2. Experimental
2.1. Coal samples
This experiment takes Mongdong lignite as the research object. Before the experiment, the coal sample was firstly dried and crushed, and the coal with particle size less than 0.15mm was screened out and put into an airtight bag for storage. Weigh 20.00±0.02 g coal sample, put it in a vacuum drying oven, dry it at 65 °C for 12 h, and get 1# coal sample. The industrial analysis of coal samples is shown in table 1.

| Coal sample | Mad/% | Vad/% | Aad/% | C_ad/% |
|-------------|-------|-------|-------|--------|
| 1#          | 14.3  | 28.9  | 4.8   | 52.0   |

Table 1 Industrial analysis of coal samples
2.2. Catalyst materials and preparation method
In this experiment, coprecipitation method was selected to prepare the catalyst. The specific steps were as follows: According to Ca/Fe ratio of 3:1, 6:1, 9:1 (the ratio of the amount of material), as seen in table 2, take corresponding quality Ca(NO₃)₂•4H₂O and Fe(NO₃)₃•9H₂O, then take a certain amount of Al(NO₃)₃•6H₂O and CO(NH)₂, and add 100 ml deionized water. All of them were fully stirred to dissolve. The conical flask containing mixture was put into the oil bath pot and stirred vigorously by electromagnetically stirring way from ambient temperature to 120 °C. And take it out after 4 h to filter when it was cooled. Subsequently, the solid should be drying 8h in a vacuum drying oven where the temperature was 80 °C. Then it was placed in a muffle oven and burned at 875 °C for 4 h. After cooling, take it out and put into a sealed bag for later using.

Table 2. Name and number of catalyst

| catalyst            | Fe/Ca | Sample |
|---------------------|-------|--------|
| 3Ca/Fe@Al₂O₃        | 3:1   | 5#     |
| 6Ca/Fe@Al₂O₃        | 6:1   | 6#     |
| 9Ca/Fe@Al₂O₃        | 9:1   | 7#     |
| 12Ca/Fe@Al₂O₃       | 12:1  | 8#     |

2.3 Experimental equipment and methods
The experiment was carried out in a modified Galanz P70D20TL-D4 microwave oven with a resonant cavity size of 220×200×180 mm, magnetron model of M24FB-610A and rated output power of 700 W. Weigh a certain amount of 1# coal sample and catalyst and grind them evenly in a mortar according to table 2. Accordingly weigh 3.5 g sample in the quartz reactor for each pyrolysis experiment. The upper part of the samples was covered with quartz cotton with a diameter of 40 mm and a thickness of 20 mm. The purpose was to prevent the coal powder from entering the subsequent pipelines along with the pyrolysis airflow and causing the pipeline blockage. Before the experiment control N₂ flow rate of 250 ml/min, scavenging for 10 minutes, then the flow control for 25 ml/min, start the microwave oven, microwave output power setting of 700 W, pyrolysis gas through condensing unit, in turn tar filter unit, gas drying device, the gas sampling by aluminum foil bag collection, every 2 minutes to replace an air pocket, collect altogether seven times, the pyrolysis time about 14 min, the gases in the air pocket product first collected by drainage method measuring different times gas volume(Vᵢ). Then, Gasboard-3100 gas component analyzer (Wuhan Sifang Photoelectric) was used to measure gas volume fraction(xᵢ). CO₂, CO and CH₄ were detected by infrared sensor, H₂ was detected by thermal conductivity sensor, and the detection accuracy was ±1%. The output of corresponding components was calculated according to equation (1).

\[
γᵢ = \frac{\sum Vⱼ xⱼi}{m_{daf}}
\]  

(1)

Average gas generation rate in different time periods was calculated according to equation (2), where mₘₐₜₙ was the dry ash-free mass of coal sample:

\[
vᵢ = \frac{γᵢ}{t}
\]  

(2)

3. Results and discussion
3.1 Pyrolysis gas generation characteristics
Average generation rates of CO, CO₂, CH₄ and H₂ in different time periods were shown in figure 1. Different proportions of Ca/Fe catalysts have a significant impact on the release process of H₂. H₂ was generated in 5# and 8# coal samples within 0-2 min, among which 5# coal sample reached the maximum
H₂ production rate in the pyrolysis process, which was 50.3 ml•g⁻¹•min⁻¹, and 8# coal sample reached the maximum H₂ production rate within 2-4 min, which was 59.9 ml•g⁻¹•min⁻¹, and then gradually decreased. The peak shape of the change curve of H₂ production rate of 6# coal sample was relatively sharp, and the peak rate was the highest of the five coal samples, 66.9 ml•g⁻¹•min⁻¹, and then gradually decreased, which was an explosive H₂ production process. The change trend of H₂ production rate of the 1# and 7# coal samples was similar. Compared with the 6# coal samples, the peak shape was relatively mild. The H₂ production rate first gradually increased to the peak value of 39.8 ml•g⁻¹•min⁻¹ and 53.3 ml•g⁻¹•min⁻¹, respectively, and then gradually decreased. By analyzing the H₂ generation rate curve, it can be seen that 3Ca/Fe@Al₂O₃ and 12Ca/Fe@Al₂O₃ make the H₂ process advance, and the addition of these three catalysts was improved because the temperature changes in the material within 0-2 min. The dielectric constant and dielectric loss factor of the material enable the material to be well coupled with the microwave field, reduce the ineffective reflection of the microwave, efficiently convert the electromagnetic energy into internal energy, and quickly reach the temperature required for pyrolysis, which improved the energy use efficiency. The rate of CO production was similar to that of H₂. In the process of CO₂ release, except for 5# and 8# coal samples, the CO₂ release of all other coal samples was concentrated in 2-4 min. Among them, the CO₂ generation rate of 6# coal sample was the highest among 5# coal samples, which was 11.2 ml•g⁻¹•min⁻¹. In addition, in the middle and late stage of pyrolysis (4-8 min), 1# coal sample still has an obvious CO₂ release process. The 5# and 8# coal samples reached the maximum CO₂ release rate within 0-2 min, which were 5.8 ml•g⁻¹•min⁻¹ and 4.8ml•g⁻¹•min⁻¹, respectively. After 4 min, there was no obvious CO₂ release sign, and the CO₂ generation process basically ended. By comparing the CO₂ release rate curves of 1# and 7# coal samples, it can be seen that they have almost the same CO₂ release rate between 0-4 min. However, after 4 min, the material enters the constant temperature range, and the CO₂ generation rate of 7# coal sample slowed down significantly, which may be caused by the reaction of CO₂ generated by pyrolysis and CaO in the catalyst, leading to the reduction of CO₂ collected. The release law of CH₄ was similar to that of CO₂.

The total production of CO, CO₂, CH₄ and H₂ was shown in figure 2. The catalysts with different Ca/Fe ratios all improved the production of H₂ and CO. The production of H₂ was in order from low to high: 8#>5#>7#>6#>1#. And the yield was respectively 310.7 ml•g⁻¹, 300.2 ml•g⁻¹, 281.6 ml•g⁻¹, 277.9 ml•g⁻¹ and 227.5 ml•g⁻¹. The production of CO was in order from low to high:8#>5#>7#>6#>1#, and the yield was respectively 225.38 ml•g⁻¹, 223.8 ml•g⁻¹, 202.6 ml•g⁻¹, 199.5 ml•g⁻¹, and 145.5 ml•g⁻¹. The variation trend of H₂ yield with different catalysts was very similar to that of CO. The CO₂ yield of 8#
coal sample decreased by 52.7% compared with that of 1# coal sample, and the corresponding catalyst was 12Ca/Fe. As Ca/Fe increased from 3:1 to 12:1, CO₂ production showed a trend of first increasing and then decreasing, among which CO₂ production of coal sample 6# was the highest, which was 25.5 ml •g⁻¹. The highest CH₄ yield was 17.8 ml •g⁻¹ for 1# coal sample, followed by 15.5 ml •g⁻¹ and 15.3 ml •g⁻¹ for 6# and 7# coal sample, respectively. The lowest CH₄ yield was 10.4 ml •g⁻¹ and 10.3 ml •g⁻¹ for 5# and 8# coal sample, respectively.

The total gas production and the content of each component were shown in Table 3. It can be seen from the figure that the addition of catalyst increased the total gas production, and the total output of 8# coal sample gas was the highest, 559.2 ml •g⁻¹. Compared with the 1# coal sample, the CO content in the pyrolysis gas composition of the other coal samples was significantly improved, and the CO₂ content was significantly decreased, indicating that the addition of the catalyst increased the content of the effective components in the gas and improved the quality of the pyrolysis gas.

Table 3. Total gas production and relative content of each component

| Sample | CO/vol.% | CO₂/vol.% | CH₄/vol.% | H₂/vol.% | Production/(ml/g) |
|--------|----------|-----------|-----------|----------|------------------|
| 1#     | 34.8     | 6.5       | 4.3       | 54.4     | 418.1            |
| 5#     | 40.8     | 2.0       | 1.9       | 54.7     | 548.6            |
| 6#     | 38.5     | 4.9       | 3.0       | 53.6     | 518.4            |
| 7#     | 39.0     | 3.9       | 2.9       | 54.2     | 519.7            |
| 8#     | 40.3     | 2.3       | 1.8       | 55.6     | 559.2            |

Figure 2. Total production of all components

Table 4 showed the weight loss of samples before and after pyrolysis and the temperature at the end of pyrolysis experiment. It can be seen from the table that after adding the catalyst, the final temperature of the sample was improved, indicating that the addition of the catalyst increases the apparent dielectric loss factor of the sample, the material absorbing ability was enhanced, and the efficiency of converting electromagnetic energy into internal energy was improved. The temperature was the highest after adding 3Ca/Fe@Al₂O₃, and further increasing the content of Ca in the catalyst caused the temperature of the material to decrease. Compared with the 1# coal sample, the weight loss rate of the sample also increased after adding catalyst, which indicated that the volatile products increased. This was because the catalyst not only reduced the reaction activation energy, but also promoted the mutual coupling between the material and electromagnetic wave, thus promoting the generation of gas.
3.2 Semi-coke FTIR analysis
Infrared spectra of raw coal and semi-coke after pyrolysis were shown in figure 3. As can be seen from the figure, within the range of wave Numbers of 2820 cm\(^{-1}\)-2950 cm\(^{-1}\) and 1100 cm\(^{-1}\)-1780 cm\(^{-1}\), the absorption peak strength of the coal sample after pyrolysis was weakened. Including 2820 cm\(^{-1}\)-2850 cm\(^{-1}\) within the scope of the corresponding absorption peak of aliphatic hydrocarbon vibration absorption peak of \(-\text{CH}_2\) and \(-\text{CH}_3\), their strength showed that the fat in the process of pyrolysis hydrocarbon side chain fracture, fall off from the brown coal macromolecular, become volatile and escape from the system, notice that after adding catalyst, absorption peak weakened further, show that the preparation of the catalyst was catalyst for this process. 1100 cm\(^{-1}\)-1780 cm\(^{-1}\) was mainly the absorption peak of oxygen-containing functional groups such as ether bond, ester bond and carbonyl group. Compared with raw coal pyrolysis semi-coke, the absorption peak in this range was obviously weak. It was speculated that the reason was that the catalyst promoted the removal of functional groups such as carbonyl group and the reaction with \(\text{CH}_4\), increasing the content of CO and H\(_2\) in the gas products, which was consistent with the gas production data.

3.3 Tar FTIR analysis
Infrared spectra of pyrolysis tar of different coal samples were shown in figure 4. As can be seen from the figure, the positions of the peaks were basically similar, indicated that the types of chemicals in the tar were basically the same. Compared with 1# coal sample, the absorption peak intensity in the infrared spectrum of the remaining coal sample pyrolysis tar in the range of 2825 cm\(^{-1}\)-2950 cm\(^{-1}\) and 1300 cm\(^{-1}\)-1500 cm\(^{-1}\) was weakened, indicated that the fat in the tar was \(-\text{CH}_2\), \(-\text{CH}_3\), etc. Hydrocarbon side chain content was reduced [5,6]. This aspect was due to the adsorption of Fe element in the rich position of the lignite macromolecule, which led to the weakening of the chemical bond between the side chain and the host, which promoted the shedding of small molecular groups. On the one hand, the catalyst formed a hot spot under the microwave field, and the volatiles undergo secondary decomposition during the precipitation process, resulting in a decrease in the aliphatic hydrocarbon side chain and an increase in gas production in the tar. The 5# coal sample pyrolysis tar has an obvious absorption peak at 750 cm\(^{-1}\), which corresponded to the out-of-plane bending vibration of four adjacent H in the aromatic ring, indicating that 0.03Ca/Fe@Al\(_2\)O\(_3\) catalyst promoted the transfer from H to tar. The degree of polycondensation of the aromatic compound in the tar was lowered, and the number of substituents was decreased.

4. Conclusions
In the experiment of microwave pyrolysis, the addition of catalysts made the pyrolysis process advance and the final temperature rise was high, indicating that the addition of catalysts increased the apparent dielectric loss factor of materials and enhanced the coupling ability with the microwave field. All the
four catalysts inhibited the release of CO$_2$ in the microwave pyrolysis experiment, of which 12Ca/Fe had the most obvious effect. Compared with 1# coal sample, CO$_2$ production decreased by 52.7%. As the release of CO$_2$ was inhibited, the total content of CO and H$_2$ in the gas composition was increased. In conventional pyrolysis experiments, only 12Ca/Fe catalyst reduced CO$_2$ production. In the experiment of microwave pyrolysis, 12Ca/Fe catalyst has the most obvious effect on improving the production of H$_2$ and CO, with the increased rates of 36.6% and 54.8%, respectively. Compared with microwave pyrolysis, although the catalytic effect on the release of H$_2$ and CO was more obvious under conventional pyrolysis, the total production was far behind, indicating that microwave catalytic pyrolysis can improve the production of CO and H$_2$ more effectively.

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