Study on the Role of Additives in Calcination Desulfurization Process of High Sulfur Petroleum Coke

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Abstract: Due to the high sulfur content of high sulfur petroleum coke, sulfur-containing gas will be produced in the production process, reducing product quality and other problems, resulting in increased production costs and equipment corrosion. How to reduce the sulfur content of high sulfur petroleum coke is of great significance to improve the utilization rate of high sulfur petroleum coke and the sustainable development of related industries. In this paper, the desulfurization of high sulfur petroleum coke was carried out by using the additive-assisted high-temperature calcination method. It was found that the desulfurization effect of different kinds of desulfurization additives was different, among which MO1, MC2, MC1 desulfurization effect was better, and the desulfurization rate could reach 68%, 58%, 56%. After compounding the three desulfurizers, the desulfurization rate can be up to 75%, and then the influence of calcination temperature and time on the desulfurization rate was investigated. Finally, the physicochemical properties of petroleum coke before and after desulfurization were analyzed by X RD, FT-IR.

Keywords: High Sulfur Petroleum Coke; Desulfurization; Calcination; Additives; Petroleum Coke Structure.

1. Introduction

Petroleum coke is the product of thermal cracking after the separation of light and heavy oils by distillation of petroleum [1]. Petroleum coke appears as a black granular or massive solid with a metallic luster and a porous structure. Its main component is carbon, with a content of more than 80 wt%, while other components include hydrogen, oxygen, nitrogen, sulfur and metallic elements. Petroleum coke has unique physical, chemical and mechanical properties, it is a non-volatile carbide, while volatile substances and impurities (such as sulfur, metal compounds, water, ash, etc.) affect the chemical properties of petroleum coke [2]. In view of the problems such as environmental pollution, production cost increase, product quality decline and serious corrosion of production equipment in the current process of high-sulfur coke utilization, an economical and efficient method to remove sulfur in high-sulfur petroleum coke is sought to alleviate the dilemma of short supply of low-sulfur coke and large quantity of high-sulfur coke. It also has important value and significance for the sustainable development of petrochemical, carbon, aluminum electrolysis and other industries and various fields related to petroleum coke.

The amount of sulfur content is a key indicator of the quality of petroleum coke. According to the different sulfur content in petroleum coke, petroleum coke can be divided into high sulfur coke (sulfur content greater than 3%), medium sulfur coke and low sulfur coke (sulfur content less than 1.5%). In the current market, the selling price of high sulfur petroleum coke is only 50%-70% of low sulfur coke. Sulfur in petroleum coke is divided into organic sulfur and inorganic sulfur [3]. Organic sulfur can be removed at low temperatures, and inorganic sulfur needs to be volatilized and decomposed at high temperatures. Sulfur in petroleum coke mainly exists in the form of organic sulfur and inorganic sulfur, of which the vast majority is organic sulfur (≥99%). Inorganic sulfur is mainly in the form of pyrite sulfur (FeS_2), and sometimes there are a small amount of sphalerite (ZnS), galena (PbS), magnetite pyrite (Fe_7S_8) and other metal sulfides in the form of [4].

Petroleum coke desulfurization is a complex process because the structure and existence state of organic sulfur have not been clearly studied. The main forms in which organic sulfur exists are primarily thiophene and thiophene derivatives bound in C-S bonds [5]. Thiophene sulfur groups exist in petroleum coke in several different forms, including on the aromatic carbon skeleton, on the side chain of aromatic molecules or naphthene side chain, and on the surface of aromatic tablets or aggregate molecules. These thiophene-containing sulfur groups can be present on the coke surface or in the pores of the coke by capillary condensation, adsorption, or chemisorption. Figure 1 below shows the possible molecular structure of sulfur in petroleum coke:

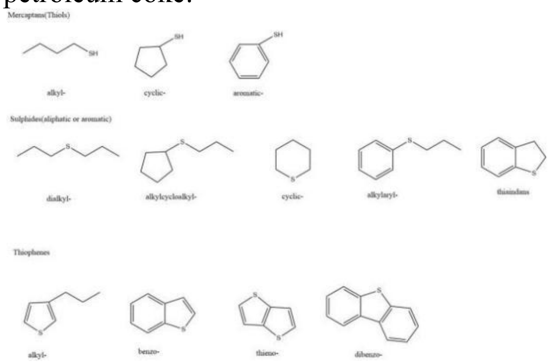

Figure 1. Forms of Sulfur Compounds Present in Petroleum Coke

At present, there is no unified standard for the quality evaluation of petroleum coke in the world. In 1992, China Petroleum and Chemical Corporation formulated the industry standard SHT0527-1992. In 2010, China Petroleum and Chemical Corporation petroleum coke enterprise standard Q/SHPRD392-2010 was formulated. Table 1 below shows the quality standards of petroleum coke.

Table 1. Quality Standard Table of Petroleum Coke (Q/SHPRD392-2010)

Petroleum coke composition item	Quality index						
	Firsts	NO.1		NO.2		NO.3	
		A	B	A	B	A	B
Sulphur content /%	≤0.5	≤0.5	≤0.8	≤1.0	≤1.5	≤2.0	≤3.0

It can be seen from Table 1 that petroleum coke is divided into three categories: grade 1, qualified products and unqualified products, among which qualified products are further divided into six categories: 1A, 2B, 2A, 2B, 3A and 3B according to the sulfur content. Low-sulfur coke is mainly used in the steelmaking industry to make ordinary power graphite electrodes, and is also suitable for aluminum refining industry as carbon for aluminum. Medium-sulfur coke is generally used as electrode paste and electrode production for electrolytic cells in the aluminum industry. In aluminum electrolysis production, every ton of prebaked anode consumes 840kg of medium-sulfur petroleum coke, and every ton of aluminum consumes 484kg of petroleum coke [6]. Therefore, medium-sulfur petroleum coke plays an important role in the aluminum electrolysis industry, and is also an important means of production. High-sulfur coke is used to produce silicon carbide (abrasive) and calcium carbide (calcium carbide), as well as other carbon products, and is also used in the manufacture of anode base blocks for aluminum smelting electrolysis tanks and in the carbon lining bricks of blast furnaces or in the construction of furnace floors [7].

Currently the main research directions are high temperature calcination desulfurization, solvent extraction desulfurization, wet chemical desulfurization, alkali metal compound desulfurization and other methods [8]. Among them, the high temperature calcination desulfurization method refers to the method of petroleum coke being calcined at a high temperature so that the sulfur in it escapes in the form of gas. A researcher conducted a high temperature calcination study on petroleum coke and found that petroleum coke showed significant desulfurization when the calcination temperature was higher than 1450°C, and the desulfurization rate increased as the temperature increased, and the desulfurization rate of petroleum coke could reach more than 90% when the temperature reached 1650°C [9]. Another study explored the effects of different temperatures and holding times on the desulfurization rate of petroleum coke, and the results showed that when the calcination temperature reached 1200°C, petroleum coke began to show obvious desulfurization effects, and the desulfurization rate increased significantly when the temperature was increased to 1500°C. In addition, prolonging the desulfurization time can also significantly improve the desulfurization rate of petroleum coke, and compared with increasing the temperature, prolonging the holding time is more direct and obvious for the improvement of the desulfurization rate. Domestic research results show that at the normal calcination temperature (1300°C) [10], the sulfur removal rate of petroleum coke is less than 10%, only by increasing the calcination temperature to more than 1500°C can reach 80% sulfur removal rate, and more than 1650°C can completely remove sulfur [11]. The high temperature calcination desulfurization method requires very high temperatures to completely remove sulfur from petroleum coke.

In the use of high temperature calcination desulfurization method can also be mixed with alkalis, oxides and other compounds as desulfurizers within petroleum coke for assisted desulfurization. Li Ning [4] et al. added metal powders such as manganese powder and iron powder to petroleum coke and obtained 52% and 20% desulfurization rate at 700℃, which proved that the metal powders have certain desulfurization effect. Zhang Chunjuan [12] et al. found that the desulfurization and sulfur fixation reaction occurs on the surface of CuO under oxygen-rich conditions and a certain temperature, and the metal oxides will form various metal sulfides with S atoms removed from the coal pyrolysis system, which has a good sulfur fixation effect on the desulfurization reaction.

Alkali metal desulfurization method is generally a petroleum coke desulfurization method by adding alkali metal compounds such as Na_2CO_3, KOH and so on to petroleum coke at a certain temperature and pressure. Habib Shlewit et al. found that desulfurization rate could reach about 70% by adding Na_2CO_3 to petroleum coke and calcining it at a high temperature of 1000°C [13]. He Xiaocai et al. found that the final desulfurization rate of petroleum coke can reach about 90% by soaking petroleum coke with NaOH solution at 0.5MPa and 160℃ [14]. The principle of desulfurization reaction of alkali metal compounds is that at a certain temperature, the desulfurizing agent undergoes changes such as melting or decomposition, and the alkali metal compounds in the molten state react with the sulfur-containing substances contained in high-sulfur petroleum coke, and the sulfur elements in the high-sulfur coke and the alkali metal compounds or their high-temperature decomposition products to generate soluble sulfide or sulfide sulfate, and then through the post-processing such as washing or acid washing can remove the soluble sulfide, so as to achieve desulfurization. Through post-processing such as water washing or acid washing, the soluble sulfide can be removed, so as to achieve the purpose of desulfurization.

The current desulfurization methods reported in the literature have excessively high calcination temperatures and high energy consumption, so it is of great importance to reduce the calcination temperature and conduct research on desulfurization by additive-assisted calcination at relatively low temperatures.

2. Experimental Sections

2.1 Experimental Steps

The experimental process of auxiliary calcination desulfurization is as follows: the desulfurization auxiliary used in the experiment is weighed in proportion, and the desulfurization auxiliary is fully mixed with petroleum coke and put into the crucible. Put the crucible into the tube furnace, open the air valve, and let in nitrogen. Set the experimental temperature and start the desulfurization experiment. After the predetermined reaction time is over, the gas is turned off, the sample is taken out for washing and drying, the sulfur content of petroleum coke after reaction is measured, and the desulfurization rate of petroleum coke is calculated. Figure 2 shows the schematic diagram of the high-temperature calcination desulfurization experimental device.

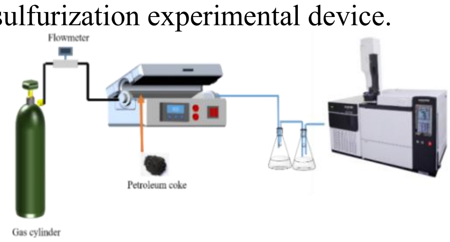

Figure 2. Evaluation Unit Diagram of Desulfurization by High Temperature Calcination

2.2 Methods for Determination of Sulfur Content

The sulfur meter purchased by this laboratory is JZDL-9000A high precision microcomputer automatic sulfur meter produced by Jingzhong Technology Co., LTD. The instrument is designed according to the national standard GB/T214-1996 Coulometric titration method. The sample is put into the sulfur meter, and the petroleum coke is burned in the purified air flow at 900℃. All forms of sulfur in the petroleum coke are burned and decomposed, and taken by the air flow to the electrolytic cell to combine with water to produce H_2SO_3. Since it destroys the dynamic balance of the original iodine-iodine ion pair in the electrolytic cell, the instrument immediately output current to electrolyze the potassium iodide solution to produce iodine, to restore the original dynamic balance. By measuring how much current is used to restore the original dynamic balance, the microprocessor measures and calculates how much sulfur is burned and decomposed in the petroleum coke, and finally the total sulfur content in the petroleum coke can be obtained, and the difference between two measurements is not more than 5%.

The petroleum coke desulfurization rate is calculated as follows:

$$Y=(S_0-S_1)/S_0\times100\% \quad (1)$$

Where: Y is the desulfurization rate; S_0, S_1 is the sulfur content of petroleum coke feedstock before and after desulfurization treatment.

3. Results and Discussion

Most of the organic sulfur in petroleum coke is thiophene, which is stable because thiophene sulfur groups are connected with petroleum coke carbon skeleton. Under high temperature conditions, C-S bond breaks and sulfur spills into gas form. At the same time, adding alkaline compounds and other catalytic substances at high temperature can effectively remove thiophene organic sulfides from petroleum coke. Li Ning [4] et al. found that metal powder to petroleum coke has some desulfurization effect at high temperature. Zhang Chunjuan [12] et al. found that metal oxides have desulfurization-sulfur fixation effect under oxygen-rich condition and certain temperature. Therefore, in this paper, from oxides, sulfates and carbonates, alkali, chloride, metal elements of the four categories of additives with better effects; Then the desulfurizer was mixed in different proportions to carry out auxiliary desulfurization experiment. Finally, the influence of calcination temperature and calcination time on desulfurization rate was studied.

3.1 Single Additive-Assisted Calcined Desulfurization

Through literature investigation and previous studies, it was found that the addition of additives with a mass fraction of 20% at 900℃ for 90min has a good desulfurization effect. The following experiments were carried out under the conditions that the calcination temperature of was 900℃, the calcination time of was 90min, and the amount of additive was 20%.

Table 2 shows the desulfurization rate of petroleum coke with different additives. It can be seen from the table 2 that MC1, MC2 and MO1 have the best desulphurization effect, with desulphurization rates of 56%, 58% and 68.93% respectively. The desulphurization effect is obviously better than that of oxides, sulfates, chlorides and metals. This may be because MC1 and MC2 reach the melting point and become molten when the calcination temperature is 900℃. At the same time, at 900℃, carbonate decomposition reaction occurs to produce metal oxides with strong oxidation. Metal oxides react with sulfur in petroleum coke to form metal sulfate, thus achieving the effect of desulfurization. At 900℃, MO1 is in a molten state, which can be fully in contact with petroleum coke. At the same time, as a strong alkaline agent, MO1 is easy to combine with sulfur-containing free radicals generated by the pyrolysis of organic sulfide, and generate small molecular gases such as H_2S to escape from the coke, thus promoting the escape of sulfide and rapidly reducing the total sulfur content of petroleum coke.

The poor desulfurization effect of chloride, sulfate, metal monomers, and oxides as additives on high sulfur petroleum coke may be due to their lack of assisting effect on the C-S bond breaking reaction in petroleum coke, or poor assisting effect, and the melting points of copper oxide, calcium oxide, and magnesium oxide are 1446°C, 2572°C, and

2852°C, respectively, and the oxides are in the form of solids when the calcining temperature is 900°C, and they have not been in petroleum coke in full contact to react. In the experimental process, it was found that chloride, metal monomers, oxides and other metal monomers generated by high temperature decomposition as well as metal compounds are difficult to be completely removed in the post-treatment, or remove higher cost, and chloride will be decomposed at high temperature to produce chlorine gas pollution of the environment. After comprehensive analysis, the best desulfurization effect was selected as MC1, MC2, MC3, MC4, MC5, MC6 and MC7. The additives were MC1, MC2 and MO1.

Table 2. Desulfurization Rates of Petroleum Coke with Different Additives

additive	desulfurization rate /%	additive	desulfurization rate /%	additive	desulfurization rate /%
$CuSO_4$	12.11	CuCl	19.43	Cu	26.87
$Fe_2(SO_4)_3$	14.25	$FeCl_3$	13.85	Sn	15.14
$Na_2 SO_4$	10.82	$MgCl_2$	12.29	Al	12.19
$CaSO_4$	7.71	$SnCl_4$	9.38	Zn	12.14
MO1	68.93	$CoCl_2$	7.05	Fe	4.03
MO2	39.27	$CaCl_2$	5.88	CuO	2.29
LiOH	20.02	KCl	2.03	CaO	1.26
$Al(OH)_3$	14.21	$ZnCl_2$	0.85	MgO	1.93
$Mg(OH)_2$	2.93	$CuCl_2$	0.36	MC1	56.89
$Zn(OH)_2$	1.53	NaCl	0.36	MC2	58.22

3.2 Composite Additives Auxiliary Calcined Desulfurization

The three additives with the best desulfurization effect were selected and mixed according to the mass ratio of 1:1, the mass addition amount of composite additive was 20%, and the calcination temperature was set to 900°C and the calcination time was set to 90min. Table 3 shows the desulfurization rate of high sulfur petroleum coke under different composite additives. As can be seen from the table, the compound desulfurization rate of MO1 and MC2 compound additive is 74.93%, and its desulfurization effect is higher than that of a single additive. This may be because MO1 melting provides an alkaline environment, which enhances the catalytic effect of carbonates on C-S bond breaking and promotes the conversion of thiophene sulfur groups in petroleum coke into more easily removed sulfoxide.

Table 3. Desulfurization Rate of Petroleum Coke with Compound Additives

number	compound additives	calcination temperature /°C	Calcination time /min	desulfurization rate /%
1	MO1+MC1	900	90	57.11
2	MO1+MC2	900	90	74.93
3	MC2+MC1	900	90	60.80

3.3 MO1 Mixed with MC2 in Different Ratios High Temperature Calcined Desulfurization

The effect of the mixing ratio of MO1 and MC2 on the desulfurization rate of petroleum coke was further explored. Figure 3 shows the desulfurization rate of petroleum coke after high-temperature calcination of the composite additive MO1 mixed with MC1 at different mass ratios. From Fig 3, it can be seen that the desulfurization rate of petroleum coke increased gradually with the decrease in the mass ratio of the composite additive MO1 to MC2, and the highest desulfurization rate of petroleum coke, 80.45%, was observed when the mass ratio of 1:2. As the mass ratio was further improved, the desulfurization rate of petroleum coke decreased, which may be due to the decrease in alkaline environment provided by the molten MO1, decreasing the catalytic effect of carbonate for the C-S bond breaking reaction.

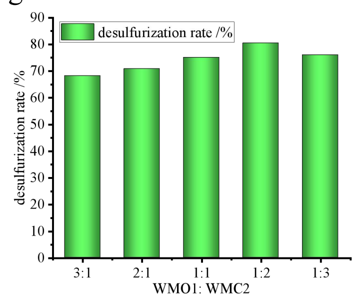

Figure 3. Desulfurization and Desulfurization Rate of MO1 Mixed with MC2 in Different Ratios at High Temperature Calcination

3.4 Effect of Calcination Temperature on the Desulfurization Rate of Petroleum Coke

Fig. 4 shows the desulfurization rate of high sulfur petroleum coke after the addition of the composite additive with the mass of MO1 and the mass of MC2 of 1:2, and the calcination of petroleum coke at 600°C, 700°C, 800°C, 900°C, and 1000°C at for 90 min, respectively. It can be seen from the figure that the petroleum coke desulfurization rate showed a trend of first steady and then increasing and then decreasing with the increase of calcination temperature. When the calcination temperature of was 600-700°C, the petroleum coke desulfurization rate was basically unchanged. When the calcination temperature is 700-900℃, the desulfurization rate of petroleum coke shows an obvious increasing trend, the highest being 80.45%. Experimental studies show that the main reason for this phenomenon is: when the calcination temperature is lower than 700℃, the main structure of petroleum coke basically does not change, thiophene sulfur-containing groups are basically not destroyed, so the rate of desulfurization is relatively low; the temperature reaches 900℃, desulfurization agent began to melt decomposition to generate oxides with strong oxidizing properties and sulfur reaction; the temperature reaches 900℃, the petroleum coke graphitization degree increases, the C-S bonds are broken in large quantities, sulfur-containing groups are destroyed, and sulfur is precipitated in the form of hydrogen sulfide and sulfur dioxide and other gases. With the further increase of calcination temperature, the desulfurization rate of petroleum coke did not increase significantly, this is because the thermally unstable mercaptans and some thiophenes in petroleum coke have already been removed, and the cleavage of the thermally stable thiophenes in petroleum coke requires a higher calcination temperature.

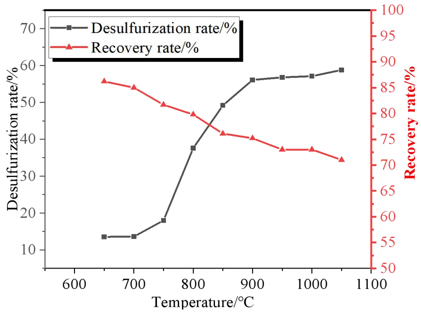

Figure 4. Desulfurization Rate of Petroleum Coke at Different Calcination Temperatures

3.5 Effect of Calcination Time on Desulfurization Rate of Petroleum Coke

Fig 5 shows the desulfurization rate and recovery rate of high-sulfur petroleum coke after calcination for 30, 60, 90, 120 and 150min at 900℃ respectively. It can be seen from the figure that when calcination time is 30min, the desulfurization rate of petroleum coke is low, and with the increase of calcination time, the desulfurization rate of petroleum coke shows a trend of increasing first and then gentle. When the calcination time is 30-120 min, the desulphurization rate of petroleum coke increases faster, and when the calcination temperature is 120 min, the desulphurization rate of petroleum coke is 82.43%. This may be because in calcination reaction at the beginning of the petroleum coke will produce a certain amount of tar, when the calcination time is shorter, the tar is too late to occur secondary pyrolysis reaction, blocking the pores of the petroleum coke, resulting in petroleum coke cracking sulfur components can not be released into the environment, resulting in a low rate of petroleum coke desulfurization, with the prolongation of the calcination time of , the tar occurs in a secondary pyrolysis reaction, so that some of the pore space of the petroleum coke is opened, the sulfur components on the surface of the petroleum coke is released, and the sulfur components of petroleum coke surface is released. The sulfur fraction on the surface of petroleum coke was released, and the desulfurization rate of petroleum coke increased. With the extension of the burning time of, the recovery rate of petroleum coke decreases, taking into account the energy consumption, recovery rate and other factors, the best burning time was selected as 120min.

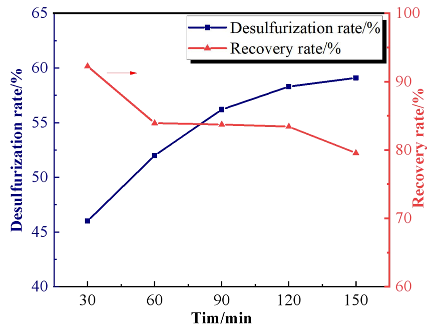

Figure 5. Desulfurization Rate of Petroleum Coke Under Different Calcination Time

3.6 Characterization of Petroleum Coke Structure before and after Desulfurization

Fig 6 shows the infrared spectrum of petroleum coke before and after desulfurization by high-temperature calcination. It can be seen from the figure that after high-temperature calcination, the absorption peaks representing the thiophene C-H bond at 3027cm^{-1} and 1309cm^{-1} disappear, indicating that the addition of additives can remove part of thiophene sulfur. The absorption peak of C-S stretching vibration on thiophene ring is at 864cm^{-1}. In the figure, the absorption peak of petroleum coke at 864cm^{-1} after high temperature calcination is significantly weakened, indicating that part of organic sulfur can be removed after calcination. The stretching vibration of -SH at 478cm^{-1} indicates that the petroleum coke contains mercaptan organic sulfur. The absorption peak of -SH near 478cm^{-1} almost disappeared, indicating that mercaptan organic sulfur in petroleum coke was basically completely removed, and the mercaptan organic sulfur could be effectively removed by calcination.

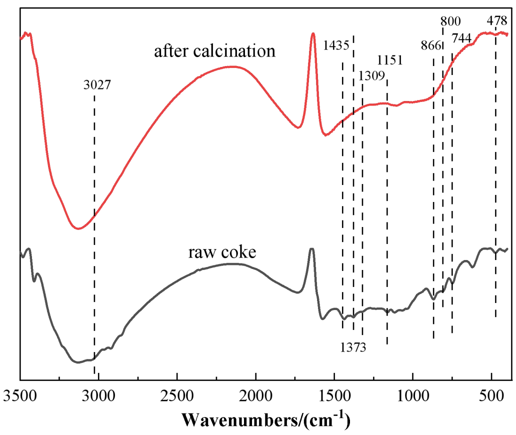

Figure 6. FT-IR spectra of Petroleum Coke before and after Desulfurization by Calcination

Figure 7 shows the XRD spectra of petroleum coke before and after desulfurization by high temperature calcination. As can be seen from Fig. 6, the petroleum coke before and after desulfurization all showed distinguishable diffraction peaks near 2θ of 25° and 43°, but the intensity of the diffraction peaks was different. The (002) peak near 2θ≈25° represents the degree of orientation of the aromatic lamellae in the microcrystals, and the (100) peak near 2θ≈43° represents the size of the aromatic carbon network in the microcrystals, and the higher and narrower (002) peaks indicate the better degree of orientation of the lamellae, and the higher and narrower (100) peaks indicate the higher degree of condensation of the aromatic nuclei. After the desulfurization of petroleum coke (002) peaks become broader, (100) peaks become obvious, indicating that the structure of petroleum coke changes after high temperature calcination, this is because in the process of calcination, additives stronger diffusion ability can penetrate into the petroleum coke interior, accelerate the decomposition of thiophene sulfide with high aromatic degree, and at the same time and pyrolysis produced by small molecule sulfide generation of inorganic sulfide to prevent the surface of the petroleum coke organic matter on the capture of small molecule sulfide after condensation, thus promoting the removal of internal sulfur components, petroleum coke heteroatoms and volatile components removal, the internal structure of petroleum coke from disorder to order. At the same time, it generates inorganic sulfide with small molecule sulfide generated by pyrolysis, prevents organic matter on the surface of petroleum coke from condensing after capturing small molecule sulfide, thus promoting the removal of sulfur component inside petroleum coke, and removing heteroatoms and volatile components in petroleum coke, so that the internal structure of petroleum coke becomes orderly from disorder.

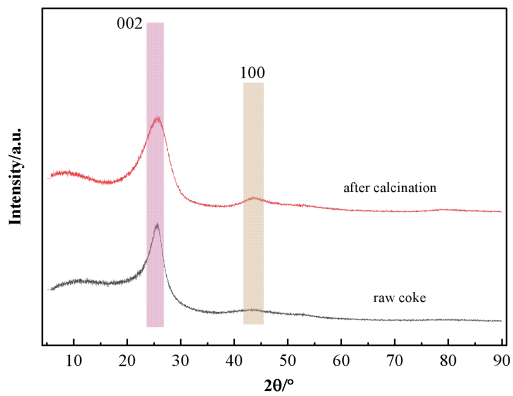

Figure 7 XRD Pattern of Petroleum Coke before and after Calcination Desulfurization

4. Conclusion

(1) In the same conditions screened which

several types, 32 kinds of desulfurization agent, comparison found which MO1, MC2, MC1 desulfurization effect is very good up to 68%, 58%, 56%.

(2) The three desulfurizers of were mixed into a composite desulfurizer at a certain ratio to investigate the desulfurization effect, and it was found that the desulfurization rate could reach 77% when the mixing ratio of MO1 and MC2 was 1:2.

(3) Based on composite desulfurizer, the effects of calcination temperature and calcination time on the desulfurization rate were investigated, and 900°C and 120 min were selected as the optimal desulfurization conditions by integrating the factors of energy consumption and cost.

(3) Infrared spectra show that found that auxiliary-assisted calcination mainly removes mercaptan sulfur and part of thiophene sulfur ; XRD spectra show that, after the desulfurization of auxiliary-assisted calcination , with the removal of sulfur and volatile components in petroleum coke, the internal structure becomes more orderly.

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