Experimental Analysis of Desulfurization and Denitrification Effect of Activated Carbon Fiber Modified by Low Temperature Plasma

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Keywords: Low Temperature Plasma; Activated Carbon Fiber; Desulfurization and Denitrification

Abstract: The surface of activated carbon fibers was modified by discharge plasma. The adsorption and catalysis of SO2 and NO on activated carbon fibers were enhanced by changing the chemical functional groups of activated carbon fibers. The trend of SO2 adsorption per unit time of activated carbon fibers before and after modification was discussed. During the modification process, the specific surface area and the pore volume of the activated carbon fiber are significantly increased, which helps to improve the adsorption performance of the activated carbon fiber. Under the action of physical adsorption and chemical adsorption, the modified activated carbon fiber has improved the effect of desulfurization and denitrification. The test results show that 8kV is the best modified voltage. After modification, the desulfurization and denitrification effect is obviously improved. The SO2 removal rate is increased from 90% to 95%, and the NO removal rate is increased from 35% to 60%.

1. Introduction

Low temperature plasma modification technology is to generate a large number of charged particles, excited state particles, photons, free radicals and other plasmas through corona discharge in a gas medium, and utilize these high energy plasmas to impact the surface of materials [1]. Activated carbon fiber is a new type of porous adsorption material, and its micropores are uniformly distributed on the surface of the fiber. Compared with activated carbon, activated carbon fiber has small and uniform pore diameter, simple structure, fast adsorption rate for small molecular substances, high adsorption rate and easy desorption. Activated carbon fibers have large specific surface area and abundant micropores, with micropore volume accounting for more than 90% of the total pore volume [2]. Activated carbon fibers have greater adsorption capacity and faster adsorption kinetics than granular activated carbon. All along, the researchers have explored various modification methods to increase the specific surface area of activated carbon fibers and enhance the activity of surface functional groups in order to improve the adsorption performance of activated carbon fibers [3]. Activated carbon fiber is used for desulfurization. It not only has the above-mentioned congenital advantages, but also can recover sulfur resources through the regeneration of activated carbon fibers while controlling atmospheric pollution. In this experiment, low temperature plasma modification technology was used to further study the desulfurization and simultaneous desulfurization and denitrification of modified activated carbon fiber on the basis of desulfurization of modified activated carbon fiber.

2. Research Experiment

2.1. Instruments and raw materials

Smoke detector, glass rotameter, BGG DC high voltage generator, GZ-100/20 silicon rectifier high voltage control cabinet. CTP-2000K plasma discharge power supply; DBD-50 low temperature plasma discharge device; modified activated carbon fibers were analyzed and characterized by SAM X-ray photoelectron spectrometer and Nicolet 5700 Fourier transform infrared spectrometer.

SY-1500 activated carbon fiber produced by an activated carbon fiber factory used in the modification experiment has various indexes as shown in Table 1.

  DOI: 10.25236/swcas.2019.012

Table 1 Activated carbon fiber index

Model	Specific surface area/m2g	Benzene absorption/(%)	Iodine absorption value/(mg/g)	Hole volume/(ml/g)	Mean pore size/A	pH value	Ignition point/℃
SY-1500	1500-1600	50-55	1400-1600	0.7-1.5	18-23	5-7	>500

2.2. Experimental method

The activated carbon fiber is cut into square sheets of 1cm×1cm, then placed in a beaker, washed with distilled water for 3-4 times, soaked for 3h, and then placed in an ultrasonic instrument for 2h to remove organic and inorganic impurities remaining in the activated carbon fiber. Adjust N flow to 10mL/min, add high voltage power supply (5kV), and perform DBD plasma surface modification. The discharge modification device consists of needle plate electrode and applied DC high voltage. The iron plate at the bottom of the reactor is used as grounding electrode. During discharge, the activated carbon fiber is evenly spread on the bottom of the reactor, and the discharge time is controlled to be 2min. Air is pumped into the system by an exhaust fan, while SO2 is pumped into the system by a cylinder under the action of pressure difference. The SO2 concentration in the simulated flue gas is regulated by adjusting the SO2 flow rate at the cylinder outlet, and the air flow rate from the exhaust fan is controlled to control the velocity of the flue gas passing through the reactor. At the same time, the white hunger flow rate at the cylinder outlet is adjusted to simulate the concentration of each gas component in the flue gas. The gas flow passes through the glass rotor flowmeter and enters the organic glass reactor filled with activated carbon fibers. In the reactor, activated carbon fibers absorb SO2 and NO, and the purified flue gas is discharged into the atmosphere.

3. Test Results and Discussion

3.1. Penetration curves of ACF denitration modified by different voltages

The experimental conditions are set as follows: NO inlet concentration is 300mg/m3, oxygen concentration is 10%, W/Q = 3. 5 g. min/L/L (ratio of activated carbon fiber mass to flue gas flow), discharge time is uniformly determined as 6 min, discharge voltage is 6kV, 8kV and 8 kV under the same conditions, and the obtained penetration curve is shown in Figure 1.

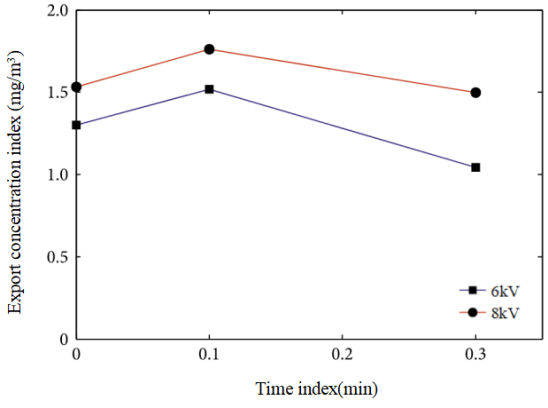

Fig.1. Punch-through koji for ACF denitration under different voltage modification conditions

After plasma surface modification for 0, 20, 40 and 80min with an output power of 130W, the ignition loss rate of activated carbon fiber gradually increased with the increase of plasma modification time, reaching 15.3%, 24.5% and 50.1% respectively. After modification, the specific surface area and pore volume of ACF are slightly reduced, but the change is not obvious, indicating that the surface structure of ACF has not been significantly changed by low temperature plasma modification. The sulfur adsorption capacity of activated carbon fiber increases with the increase of discharge modification voltage per unit time. From 5 to 8 kV, the adsorption rate of activated carbon fibers increased the fastest. Then, with the increase of discharge voltage, the sulfur adsorption rate

of activated carbon fibers changed little, and gradually became stable. Compared with that before modification, the denitrification performance of the modified activated carbon fibers has been improved to varying degrees. The initial denitrification efficiency of the modified activated carbon fibers is 52% before modification, and the initial denitrification efficiency of the modified activated carbon fibers can be increased to 74% after 8 kV modification. Carbon gasification and etching on the surface of activated carbon resulted in loss of weight and burning of activated carbon fibers. With the prolongation of modification time, the etching effect caused by plasma increases, and the burnout rate increases gradually.

3.2. NO adsorption curves modified by different voltages

The curves of NO adsorption amount after different voltage modification are shown in Figure 2. The experimental conditions are the same as those of the above penetration experiment. The adsorption time is set to 50 minutes.

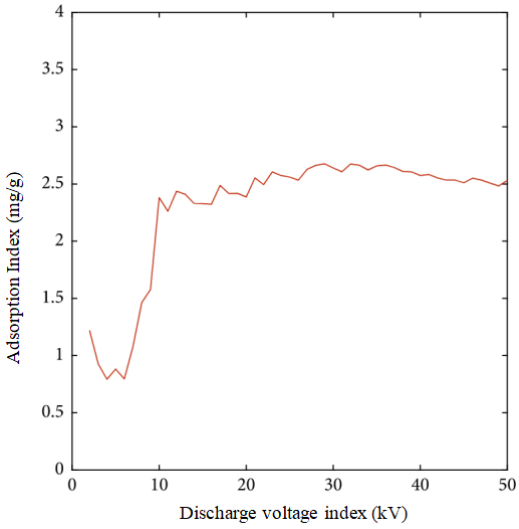

Fig.2. NO adsorption curves after different voltage modification

Generally speaking, basic functional groups have good affinity for SO2. The oxygen-containing functional groups on ACF surface are mainly divided into acidic basic functional groups and neutral functional groups, wherein the acidic functional groups include carboxyl and phenolic hydroxyl groups; Compared with the unmodified ACF, the longitudinal stripes on the surface of the ACF modified by low temperature plasma are thickened and deepened, and the surface becomes rough. The results show that low temperature plasma modification has no destructive effect on ACF surface structure. With the increase of discharge voltage, the basic functional groups on the surface of activated carbon fiber gradually increase and the acidic functional groups gradually decrease, but the total amount basically remains unchanged. The decreasing and increasing trends of acid-base functional groups are basically the same. Compared with the adsorption capacity of 18.6 mg/g of activated carbon fiber under unmodified conditions, it was increased by 75%. This result directly shows that the activated carbon fiber after modification has greatly improved the adsorption capacity of NO. This is mainly because the solid surface of the activated carbon fiber has an unsaturated structure and has unique surface chemical properties. The free radical generated by the modification process oxidizes the surface group of the activated carbon fiber, changes the morphology and distribution of the oxygen-containing functional group, and improves the activated carbon fiber. Surface properties. The removal effect of ACF on NO2 is much better than that of NO, because from the physical characteristics, NO2 is more favorable for competing for active sites on the surface of activated carbon fibers, so that it is adsorbed.

3.3. Experiment on desulfurization and denitration of ACF after plasma modification

Compared with the denitration experiment alone, the denitration efficiency of activated carbon fiber is significantly reduced when SO2 is present under the same conditions. It can be seen that the

presence of SO2 is not conducive to NO removal. In addition, the etching effect of the activated carbon fiber in the modification process increases the number of micropores, increases the specific surface area, and improves the adsorption capacity of the activated carbon fiber. Plasma modified ACF can effectively introduce nitrogen-containing functional groups to its surface, and change the morphology distribution of oxygen-containing functional groups to a certain extent, thus greatly improving the basic groups and oxidation ability of ACF surface. Modification has an effect on the active center of the ACF surface, providing more catalyst center number or active site for the catalyst. The transmittance of the absorption peak in the infrared spectrum of the ACF surface chemical functional group after discharge treatment is obviously higher than that of the undischarge-modified ACF. Polar molecules have stronger adsorption capacity than non-polar molecules and are dominant in the competition for active sites. Therefore, in the case of simultaneous desulfurization and denitrification, the denitration efficiency of the activated carbon fiber is lowered.

The performance of modified activated carbon fiber at the same time for desulfurization and denitrification has been greatly improved, mainly in the following: the breakthrough time of desulfurization after modification is further extended, and the desulfurization efficiency in the breakthrough time is improved [4]. The adsorption of activated carbon fiber is physical adsorption and chemical adsorption. Due to the introduction of a large amount of oxygen in the modification process, the acidic oxygen-containing functional groups of the activated carbon fiber surface increase, and the total acidic group increases. The discharge plasma can initiate the mutual transformation of the functional groups on the surface of the ACF and can introduce elements from the external environment into the surface of the ACF, but when the voltage is too high, the effective groups are decomposed. The modified ACF has a longer desorption time at the peak of the desorption peak, and the temperature at the peak of the desorption peak is higher than that of the unmodified one, indicating that higher desorption activation energy is required [5]. From the results of adsorption experiments and group analysis, we can know that the discharge voltage of about 8kv is a turning point for the modification of activated carbon fiber, so the activated carbon fiber samples with a discharge voltage of 8kV are taken for analysis. It is concluded that the denitration performance of activated carbon fiber has also been significantly improved. The denitration efficiency has been increased from 25%-35% before modification to 60% after modification. The outlet concentration of NO after modification is stable compared with that before modification, and remains basically unchanged for 50 minutes.

When the surface of ACF is modified by discharge plasma, the plasma acts on the surface of the sample and etches the ACF surface while introducing new groups. Different discharge times affect the range and depth of reaction on the one hand, and the type of reaction on the other hand [6]. After modification, there is no new characteristic peak in the functional group region, the absorption peak of the functional group is strengthened, and the acidic oxygen-containing functional group is increased, which can improve the NH3 adsorption capacity on the ACF surface. The surface of the unmodified activated carbon fiber has a few attachments. Although the specific composition is not clear, it is known through analysis that the carbon fiber may be generated during the activation process. The surface of the activated carbon fiber contains active groups important for desulfurization and denitrification, such as hydroxyl, ether, carboxyl, etc., while the discharge plasma-modified activated carbon fiber can further introduce a large number of oxygen-containing nitrogen-containing functional groups to the surface [7]. The increase of the acidic group will increase the surface polarity of the activated carbon fiber, which is beneficial to the adsorption of polar substances by the activated carbon fiber. As the modification time increases, the amount of nitrogen introduced will increase, and the nitrogen-containing functional groups formed on the surface of the ACF will continue to increase until the oxygen content of the ACF surface is consumed [8]. As the temperature rises, some functional groups on the surface of the ACF decompose, the surface active sites decrease, and the catalytic activity begins to decrease. The number and type of surface functional groups of the unmodified sample were small, and the conversion rate of NO was lower than that of the modified sample.

4. Conclusion

ACF has large specific surface area and contains oxygen and nitrogen functional groups. The discharge plasma treatment of ACF can effectively introduce nitrogen-containing functional groups to its surface and change the morphology and distribution of oxygen-containing functional groups. Before and after plasma modification, there is no obvious difference in pore volume and no obvious mechanical damage on the surface of ACF. Plasma modification only changes the surface properties of ACF, and has little effect on its pore structure and surface morphology. When the time of reaching the stable state is shorter, the adsorption capacity of activated carbon fibers modified by discharge increases greatly. The results show that the adsorption rate of activated carbon fibers by discharge modification is greatly increased. When activated carbon fiber is used for simultaneous desulfurization and denitration, the existence of SO2 makes the denitration efficiency very low, and after modification, the defect of too low denitration efficiency under the condition of simultaneous desulfurization and denitration can be obviously reduced, and the NO removal efficiency can be improved from 35% to 60% on the premise of promoting the sulfur dioxide removal efficiency; With the progress of modification, the oxygen-containing functional groups of activated carbon fiber increase, among which the acidic functional groups increase obviously and the basic functional groups decrease slightly, which increases the surface polarity of activated carbon fiber and is beneficial to the absorption of polar substances. Discharge time affects the modification results. The surface active substance of ACF increases with the modification time, but increases slowly after 6min. Considering comprehensively, 4min or 8min is the best modified voltage.

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