Investigation on activated semi-coke desulfurization

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Abstract: An activated semi-coke with industrial-scale size was prepared by high-pressure hydrothermal chemistry activation, HNO_3 oxidation and calcination activation in proper order from Inner Mongolia Zhalainuoer semi-coke, which is rich in resource and cheap in sale. SO_2 adsorption capacity on this activated semi-coke was assessed in the fixed bed in the temperature range of 60—170℃, space velocity range of 500—1300 h^{-1}, SO_2 concentration of 1000—3000 ppmv, and N_2 as balance. The surface area, elemental and proximate analysis for both raw semi-coke and activated semi-cokes were measured. The experimental results showed that the activated semi-coke has a high adsorption capacity for sulfur dioxide than the untreated semi-coke. This may be the result of increase of surface area on activated semi-coke and surface oxygen functional groups with basicity characteristics. Comparison to result of FTIR, it is known that group of —C—O—C— may be active center of SO_2 catalytic adsorption on activated semi-coke.

Keywords: activated semi-coke; high-pressure hydrothermal chemistry; activation; desulfurization

Introduction

The commercial methods of removal of SO_2 are wet desulfurization. The common one is wet desulfurization using limestone, which has been applied most widely in large power generation and will be employed further in the future because limestone is the cheapest and most resourceful absorbent. The capital and running costs for a current SO_2 removal plant are 800 RMB Yuan per 1 kW and 1000 RMB Yuan per ton-SO_2, respectively. But, for developing China, due to so high cost it is difficult to apply in middle or small-scale power generation. And the operation of limestone desulfurization is very complication. Therefore, people are exploring a new desulfurization method.

China is rich in coal resource. The carbon-base material desulfurization methods such as active carbon, activated coke, activated semi-coke and activated carbon fiber are taken seriously. The semi-coke among them is the most promising method in flue gas desulfurization. The reasons are: on one hand, semi-coke is a by-product of lignite gasification, that is, a product of pyrolysis in lower temperature range of 600—700℃ from lignite. The production amount of semi-coke from lignite is very large in Inner Mongolia and Shanxi Province, but its consumption amount is very small. The piled semi-coke is the same as mountain and get environmental pollute. The price of semi-coke sale is very low; on the other hand, there are many oxygen and hydrogen group on the semi-coke surface, which have absorbent properties for sulfur dioxide. Therefore, the preparation of flue gas desulfurization from semi-coke is an environmental friendly method, which is changed into product of protection of environment from the product of pollution of environment.

In early research paper, the activated semicokes from Hailaer(Liu, 1999; Li, 1998) and Baorixile(Xiong, 1998) lignite semi-coke were prepared by steam activation or N_2 containing 2% O_2 oxidation, which are traditional activation methods for activated carbon. The purpose of these activation methods is to improve the physical structure of semi-coke. The results showed that the production ratio of activated semi-coke by these activation methods was only from 50% to 60% of raw semi-coke weight and the activity of desulfurization decreased dramatically with increase of run time and semi-coke size. Therefore, exploring a new method of treatment of semi-coke instead of steam activation or partial oxidation is very important in flue gas cleanup. In this paper, the activation methods of high-pressure hydrothermal chemistry activation, HNO_3 oxidation and calcination activation of semi-coke in proper order were used to modify semi-coke with industrial-scale size in order to increase production ratio and activity of desulfurization of activated semi-coke.

1 Experimental

1.1 Preparation of activated semi-coke

The semi-coke used in the experiments was obtained from Inner Mongolia Autonomous Region, China, which was prepared from lignite by pyrolysis in the temperature range of 600—700℃. It was crushed and screened at 4—10 mesh (1—4 mm) industrial-scale size and partially dried at 120℃ prior to its use. The raw semi-coke(named sample No.1) was pre-activated in high-pressure reactor at temperature 270℃, pressure 43 atm for 4 h. After separated and dried at 120℃ for 2 h, the pre-activated semi-coke(named sample No.2) was obtained. The pre-activated semi-coke was treated at reflux in 45% wt HNO_3 for 2 h. After cooling the treated sample was separated and wash with distilled water up to neutral reaction and dried at 120℃. The oxygenated semi-coke(named sample No.3) was obtained. The oxygenated semi-coke was heat-treated by calcinations in flowing N_2 stream at temperature 700℃ for 2 h. After cooling in flowing N_2 stream the activated semi-coke(named sample No.4) was obtained.

1.2 Characterization of samples

The proximate analyses of sample were performed according to the China State Standards GB/T 212—2001 for coal and coke, and elemental compositions were analyzed by

means of an elemental analyzer system(Vario EL).

The specific area of samples was carried out by N_2 adsorption at 77 K, applying the Brunauer-Emmett-Teller (BET) equation to N_2 adsorption.

The surface basicity and acidity of the samples were measured according to the method proposed by Rubio *et al*. (Rubio, 1997). The surface basicity of the samples was evaluated by mixing 1 g of sample with 100 ml of a 0.01 mol/L solution of benzoic acid. The suspension was shaken for 24 h at room temperature. An aliquot of the supernatant liquid was then titrated with a 0.01 mol/L solution of NaOH. The same procedure was used to determine the surface acidity with diphenyguanidine (DFG) and with HCl as titration solution.

The surface group was carried out by FTIR-8100 instrument made in Japan.

1.3 SO₂ adsorption experiment

The SO_2 adsorption capacity of sample were determined by passing a flow containing 1000—3000 ppm of SO_2, 5% of O_2, 10% of water vapor and nitrogen as balance through a fixed bed of 30 ml of samples in the temperature range of 60—170 ℃, space velocity range 500—1300 h^{-1}. The

experimental installation consists of a fixed bed, device for the preparation of the gas mixture, temperature control and on-line analyses of SO_2, and O_2 concentrations. The gases N_2, SO_2, and O_2 are dosed by mass flow meters. Water vapor is introduced by gas mixture flow saturation at a desired temperature. The inlet temperature of gas mixture to the reactor is controlled. The reactor consists of a quartz tube, which has an inner diameter of 25 mm. The maximum length of the reactor is 0.8 m. The temperature within the reactor is measured by a thermocouple. The temperature in the reactor is kept constant by a furnace in contact with the outside wall of the reactor. The reactor was provided with a bypass, which allows for measure the SO_2 concentration before starting an experiment.

The concentration of SO_2 and O_2 were analyzed by Drager flue gas instrument made in Germany.

2 Results and discussion

2.1 Influence of treatment process on sample properties

Some properties of the semi-coke before and after treatment by high-pressure hydrothermal chemistry activation, HNO_3 oxidation and calcination activation are given in Table 1.

Table 1   Characteristics of the semi-coke before and after treatment by various activation methods

Sample No.	Proximate, %			Elemental composition, %				Surface properties		
	Moisture	Ash	Volatile matter	N	C	H	O	Area, m²/g	Basicity, mmol/g	Acidity, mmol/g
1	8.82	8.04	12.98	1.19	75.76	2.03	15.78	13.6	0.1856	0.0752
2	6.43	7.40	9.06	1.21	76.57	1.81	12.73	284.2	0.4697	0.0945
3	7.46	4.98	19.83	2.24	70.49	1.80	21.31	256.4	0.1185	0.1415
4	3.81	6.81	6.06	1.83	83.53	1.31	6.82	381.3	0.7189	0.2912

Table 1 shows that the special surface area of the pre-activated semi-coke is as nearly 20 times as that of the raw semi-coke after treatment by high-pressure hydrothermal chemistry. This is because that the reaction of water vapor with carbon atoms creates new micropores and expands the macropore network created during semi-coke production as well as opens block pores.

The amount of volatile matter and the oxygen content in pre-activated semi-coke by hydrothermal chemistry method decreases with activation. This is result of volatile matter partly vaporizes during high-pressure hydrothermal chemistry activation.

The surface basicity on pre-activated semi-coke is dramatically increased and the acidity slightly increased.

At high-pressure hydrothermal chemistry activation, water is a kind of solvent and also activated molecule, it differs from water vapor in steam activation at high temperature and ambient pressure, which is only activated agent. It is a mild activation. The production ratio of activated semi-coke can reach 90% by this activation in this research.

After pre-activated semi-coke was treated by HNO_3 oxidation, the treatment results in increase of the amount of volatile matter and the oxygen content of oxygenated semi-

coke. This is due to HNO_3 oxidation produces a large number of oxygenated surface groups in semi-coke, which show acidity characteristics. Therefore, the pre-activated semi-coke by HNO_3 oxidation has a higher acidity and considerably lesser basicity than pre-activated semi-coke.

The treatment by HNO_3 oxidation also leads to some decrease of the surface area of the pre-activated semi-coke. This may be a result of steric effects, caused by the surface oxygenated group preventing the N_2 molecules from entering into narrow pores, in accordance with reference (Lisovskii, 1997).

After the oxygenated semi-coke treated by HNO_3 oxidation was heat-treated by calcinations at high temperature, the activated semi-coke has a large increase of surface area and a large decrease of oxygen content. This is due to decomposition of the surface oxygenated group formed in HNO_3 oxidation. This decomposition leads to surface basicity increase and surface acidity decrease, in accordance with the experiment data.

2.2 The activity of raw semi-coke and activated semi-cokes

The SO_2 removal activity of raw semi-coke and activated semi-cokes were measured at temperature 90 ℃, space

velocity 900 h^{-1}, and atmospheric pressure. The experimental results are shown in Fig.1 and Table 2.
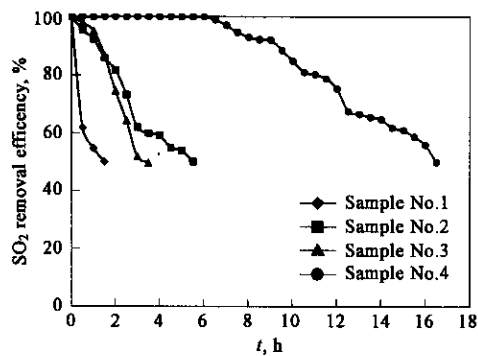
Fig.1   Desulfurization curve of raw semi-coke and activated semi-cokes

Table 2 SO_2 absorption capacities for samples

Sample No.	1	2	3	4
SO_2 absorption capacity($gSO_2/100gC$), %	1.04	3.27	2.31	8.9

As shown in Table 2 and Fig.1, the pre-activated semi-cokes have more high SO_2 removal efficiency and the amount of SO_2 adsorbed than raw semi-coke. The SO_2 removal capacity for pre-activated semi-coke by high-pressure hydrothermal chemistry activation is as 3 times as that of raw semi-coke. The hydrothermal chemistry activation mainly promotes special surface area and surface basicity on raw semi-coke. This results in the increase of SO_2 adsorption capacity on semi-coke. After the pre-activated semi-coke was treated by nitric acid activation again, the oxygenated activated semi-coke has less SO_2 adsorption capacity than the pre-activated semi-coke by high-pressure hydrothermal chemistry activation. This may be the nitric acid activation increases surface acidity and decrease surface basicity on the activated semi-coke, therefore, this results in SO_2 adsorption efficiency and capacity decrease. By the oxygenated activated semi-coke calcinated in flowing N_2 at temperature 700 ℃, the oxygenated function groups from nitric acid treatment on the oxygenated activated semi-coke were decomposed and were changed into basic group with SO_2 adsorption property. This explanation may be showed by the high SO_2 adsorption capacity for heat-treated activated semi-coke. Therefore, the surface area and basicity play an important role in promoting the activated semi-coke SO_2 removal.

2.3   The temperature influence on SO_2 adsorption capacity

The SO_2 adsorption capacity with the increase of temperature in the temperature range of 60—170 ℃ for the activated semi-coke were measured at space velocity 900 h^{-1}, atmospheric pressure, SO_2 concentration 1000—3000 ppmv, H_2O 8%, O_2 5%. The experimental results are shown in Fig.2.

Fig.2 showed that SO_2 adsorption capacity with the change of temperature has a maximum amount. The SO_2 adsorption capacity increases with the increase of reaction
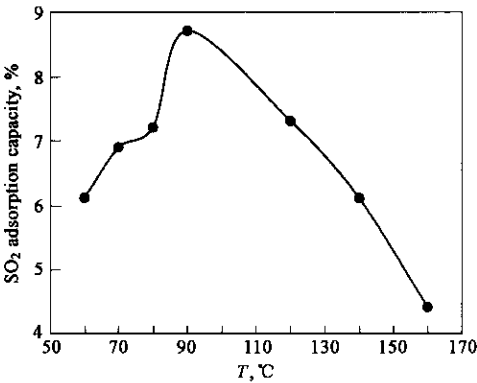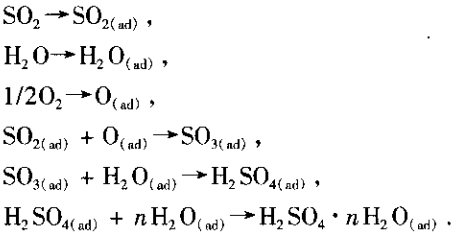
Fig.2 SO_2 adsorption capacity vs temperature

temperature from 60 ℃ to 90 ℃. And the SO_2 adsorption capacity decreases with the increase of reaction temperature from 90 ℃ to 160 ℃. This is concordance with the results obtained by Lisovskii(Lisovskii, 1997) and Li(Li, 1998). Their experimental results showed the activated carbon has the highest adsorption capacity for SO_2 at 110—120 ℃ and its adsorption capacity decrease with increase temperature.

Tamura et al. proposed the mechanism of SO_2 adsorption on activated carbon in the presence of oxygen and water vapor at about 100 ℃ as follows(Mochida, 2000):

$$SO_2 \rightarrow SO_{2(ad)},$$
$$H_2O \rightarrow H_2O_{(ad)},$$
$$1/2O_2 \rightarrow O_{(ad)},$$
$$SO_{2(ad)} + O_{(ad)} \rightarrow SO_{3(ad)},$$
$$SO_{3(ad)} + H_2O_{(ad)} \rightarrow H_2SO_{4(ad)},$$
$$H_2SO_{4(ad)} + nH_2O_{(ad)} \rightarrow H_2SO_4 \cdot nH_2O_{(ad)}.$$

The mechanism of SO_2 adsorption on activated semi-coke is the same as activated carbon. In activated semi-coke desulfurization process, the SO_2 adsorptions on activated semi-coke may be a control step in all the process. The SO_2 adsorptions on activated semi-coke are separated into both physical adsorption and chemical adsorption. Both adsorptions on activated semi-coke coexist. SO_2 was adsorbed in physical adsorption first, then SO_2 adsorbed in physical change into SO_2 adsorbed in chemical. In temperature range of 60—90 ℃, the rate of physical adsorbed SO_2 is bigger than that of chemical. The SO_2 chemical adsorption is the control step. Therefore, with the increase of temperature in range of 60—90 ℃, the amount of SO_2 chemical adsorption increase gradually. This results in SO_2 adsorption capacity increase with increasing the temperature. In temperature range of 90—160 ℃, the SO_2 physical adsorption control SO_2 adsorption. As we known, physical adsorption decreases with the increasing temperature. This results in SO_2 adsorption capacity decrease with the increasing temperature.

2.4   The space velocity influence on the SO_2 adsorption capacity

The change of SO_2 adsorption capacity for activated

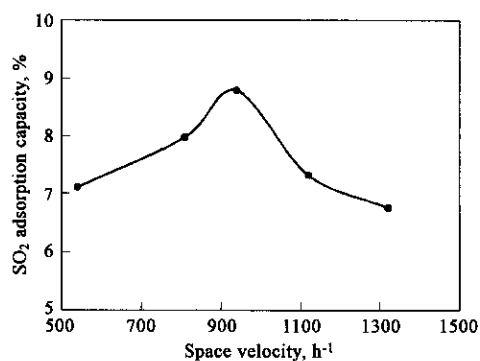semi-coke with the increase of reaction space velocity at temperature 90 ℃, atmospheric pressure are shown in Fig.3.

Fig.3   SO₂ adsorption capacity verses reaction space velocity

The SO_2 adsorption capacity increases with the increase of the reaction space velocity from 500 h^{-1} to 900 h^{-1}. At reaction space velocity 900 h^{-1}, the amount of SO_2 removal is the largest amount. And the SO_2 adsorption capacity decreases with the increase of reaction space velocity from 900 h^{-1} to 1300 h^{-1}. This appearance can reflect outside diffuse influence on SO_2 adsorption at lower space velocity on activated semicoke. When reaction space velocity is so big as to eliminate the outside diffuse influence on SO_2 adsorption, the maximum amount of SO_2 adsorption can be obtained.

2.5   The H_2O concentration influence on SO_2 adsorption capacity

From the mechanism of SO_2 adsorption, it is known that adsorbed H_2O reacts into adsorbed sulfuric acid with adsorbed SO_3. Water vapor in flue gas can influence on SO_2 adsorption. The SO_2 adsorption capacities with various amount of water vapor are shown in Table 3.

The influence of water vapor content in the flue gas on SO_2 adsorption capacity is very remarkable at water vapor content less than 5%. When water vapor content in the flue gas exceeds 5%, SO_2 adsorption capacities have little change with the increase of water vapor content.

Table 3   The SO_2 adsorption capacity verses H_2O concentration

Water vapor content in the flue gas, volume %	2	5	8
SO_2 adsorption capacity, weigh %	4.7	7.9	8.9

2.6   IR characterization

The IR experimental results for sample No.4 both before desulfurization and after desulfurization are shown in Fig.4.

Fig.4 shows that there are many adsorption bands at 3400—3500 cm^{-1}, 2900 cm^{-1}, 2300—2400 cm^{-1}, 1500—1600 cm^{-1}, 1100—1300 cm^{-1} on activated semi-coke. According to literature (Zawadzki, 1978), these adsorption bands can attribute to the following vibration: O—H stretching (3450 cm^{-1}), aliphatic C—H groups (2970 cm^{-1}), CO_2 adsorption bond(2400 cm^{-1})(Mortrra, 1983), C = O bond(1650 cm^{-1}), —C—O—C— vibration in the
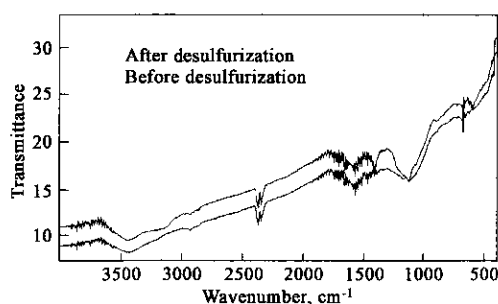

Fig.4   FTIR spectra of activated semi-coke(before desulfurization and behind desulfurization)

lactonic structure (1260 cm^{-1}). Comparison spectra of activated semi-coke before desulfurization with behind, it is also seen that beside above adsorption bands mentioned there are some adsorption bands on activated semi-coke used, such as bands at 1400 cm^{-1}, 1110 cm^{-1}. The above adsorption band is caused by SO_2 adsorbed on activated semi-coke. At the same time, while new bands appeared, the absorption bands at 1120 cm^{-1} changed in shape, namely, its peak changed to narrowband and sharp. It showed that —C—O—C— group is connected with desulfurization. —C—O—C— group is a basic functionality, and SO_2 is the acidic gas. Therefore, —C—O—C— play an important role in the SO_2 absorption. The —C—O—C— group may be the active center of the desulfurization on the activated semi-coke.

3   Conclusions

The activated semi-coke by the activation of the high-pressure hydrothermal chemistry, HNO_3 oxidation and calcinations activation has a high adsorption capacity for sulfur dioxide than the untreated semicoke. The activation increase surface area and basicity in activated semi-coke. The big surface area and basicity can promote SO_2 adsorption in activated semi-coke. The temperature, velocity space and water vapor have the best operation range to industrial-scale size activated semi-coke, the best conditions are 90 ℃, 900 h^{-1} and H_2O 8%. The group of —C—O—C— may be active center of SO_2 catalytic adsorption on activated semi-coke.

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