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The preparation of composite carrier by using diatomite and activated carbon for desulfurization in flue gas

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In this study, the diatomite and activated carbon were selected as raw materials to prepare the composite carrier for desulfurization. The orthogonal experiments were performed to optimize the preparing conditions, and the influences of the mass ratio of activated carbon to diatomite, the content of acetic acid, calcination temperature and calcination time on desulfurization performance of composite carrier were investigated. The experimental results show that the desulfurization performance of composite carrier strongly depends on the preparing conditions, and the best preparing condition was shown as follow: the ratio of activated carbon to diatomite 2:3, acetic acid 3 ml/10 g composite carrier, calcination temperature 400 °C, calcination time 3 h.

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1. Introduction

The sulfur dioxide in coal-fired flue gas is a main source of sulfur dioxide pollution in China; therefore the desulfurization in flue gas is one of the major ways for controlling SO_2 pollution. Generally the desulfurization in flue gas is carried out by wet, semi-dry or dry process [1]. At present the wet method is the most widely applied technology. However under the condition of the same desulfurization efficiency, the dry and semi-dry desulfurization processes have obvious advantages compared with the wet process in unit investment, and operating cost. Therefore the dry and semi-dry desulfurization processes have good foreground of spreading and industrialization [2]. Coal sulfur dioxide in flue gas is the main sulfur dioxide pollution in our country at present. For prevention and control of sulfur dioxide from the atmosphere is given priority to with flue gas desulfurization method. Flue gas desulfurization's methods are mainly have wet desulfurization, half dry process desulfurization and dry desulfurization. The most widely used flue gas desulfurization method is wet flue gas desulfurization, but the desulfurization efficiency under the same conditions, compared with the wet desulfurization, dry, half-dry process desulfurization have obvious advantages in unit investment, operating cost, floor area, it will also become a industrialization prospect of flue gas desulfurization technology. However, one of the most environmental protection and development potential, belong to the dry process desulfurization. The dry process desulfurization activated carbon due to its desulfurization process is simpler, with little side effects in the regeneration process and gradually getting people's attention. But sulfur capacity decrease sharply after the temperature rise of activated carbon, therefore the researching hot spot at present is how to develop the compound desulfurizer carried with activated carbon [3].

Diatomaceous earth possesses unique micro porous structure, lightweight, large specific surface area, high porosity, strong adsorption ability, good insulation effect etc, and storage is rich, and price is low [4-5]. Thus, this topic integrality the characteristics of the activated carbon and diatomite, diatomite activated carbon was prepared with strong adsorption of the new composite carrier to investigate its application in the flue gas desulfurization

2. The experiment part

2.1 The raw material

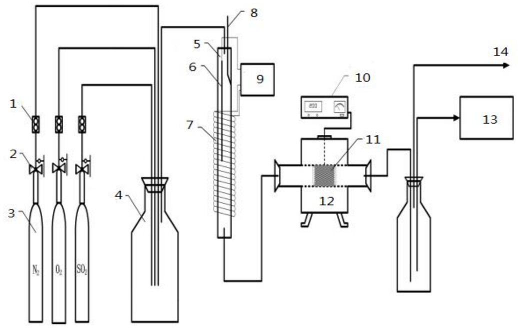
This experiment selected activated carbon and diatomite from linjiang city as raw material to prepare a new type composite carrier.

2.2 The preparation of composite carrier

Diatomaceous earth and activated carbon were grinded to 80 mesh and mixed according to certain ratio, extruded moulding by adding a certain amount of acetic acid, dried in drum wind drying oven 40 minutes at 105 °C, then calcinated in the muffle furnace, calcination temperature was 400~500°C, calcination time was 1~3 h, finally made the composite carrier.

2.3 The compound desulfurizer activity testing equipment

This desulfurization test conducted in isothermal fixed-bed reactors, the inner diameter was 25mm, and length was 50cm.Catalyst layer was placed in the tube furnace center. Catalyst performance testing equipment shown in Fig. 1.



1. gas flowmeter; 2. relief valve; 3. high pressure steel cylinders; 4. mixed gas cylinders; 5.quartz tube; 6.thermocouple; 7.heat tape; 8.water dropper; 9. temperature controller; 10. tube furnace control instrument; 11. catalyst layer; 12.tube furnace; 13. hand-held gas analyser; 14. gas emission

Fig. 1. Catalyst performance testing equipment

3. Result and discussion

3.1 The optimum preparation conditions of compound carrier

The orthogonal experiments were performed to optimize the preparation conditions with 4 factors and 3 levels design, four factors were selected different activated carbon and diatomite mixing propor tion (A), acetic acid content (B), calcination temperature (C) and calcination time (D).

The activated carbon and diatomite mixing proportion were selected: 2:3, 3:7, 1:4; the content of acetic acid in every 10g composite carrier were selected: 2 ml/10 g, 3ml/10g, 4ml/10g; calcination temperature were selected: 400°C, 450 °C, 500 °C; Calcination time were selected: 1 h, 2 h, 3h. Orthogonal experimental design shown in Table 1.

Table 1. Four factors and three levels orthogonal table

analyze project	mixing proportion（A）	acetic acid content（B）	calcination temperature（C）	calcination time（D）
1	1:4	2ml/10g	400	1h
2	1:4	3ml/10g	450	2h
3	1:4	4ml/10g	500	3h
4	3:7	2ml/10g	450	3h
5	3:7	3ml/10g	500	1h
6	3:7	4ml/10g	400	2h
7	2:3	2ml/10g	500	2h
8	2:3	3ml/10g	400	3h
9	2:3	4ml/10g	450	1h

By means of orthogonal experiment of nine kinds of composite carrier sample desulfurization performance testing to map the desulfurization rate and desulfurization time coordinate relationship, plotted by desulfurization time (min) on the horizontal axis and desulfurization rate (%)on the vertical. The test results were shown in Fig. 2.

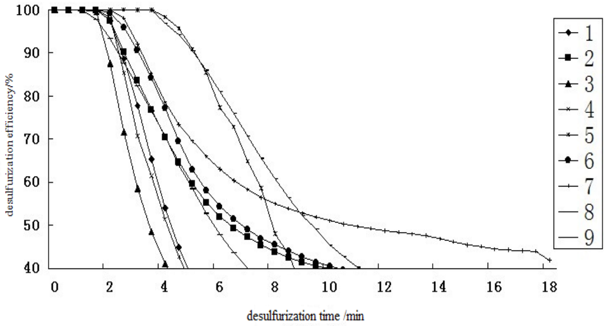


Fig. 2. The influence of different ratio of composite carrier on the desulfurization performance

It can be seen from Fig. 2, with the increase of the desulfurization time, the desulfurization rate of compound carrier gradually decreases. The time of 5th and 8th samples were longer than other samples in maintaining 100% desulfurization rate, and the 8th tendency that the desulfurization rate decreased with the increase of desulfurization time was apparently below 5th samples. So the desulfurization performance of 8th sample was better than the 5th sample. It can also be seen from Fig. 2 that 7th sample showed slowly decreased tendency in desulfurization efficiency. However, when the desulfurization efficiency was higher than 60%, the 8th sample was obviously superior to 7th samples. Therefore the optimum preparation of composite carrier was that: the proportion of activated carbon and diatomite was 2:3, acetic acid 3 ml/10 g, calcination temperature was 400 °C and the calcination time was 3 h.

3.2 The influence of different preparation factors on the desulfurization efficiency

A_1, A_2, A_3 in the table respectively represented the proportion of activated carbon and diatomite: 1:4, 3:7, 2:3; B_1, B_2, B_3 respectively represented the content of acetic acid in every per 10g: 2ml, 3ml, 4ml; C_1, C_2, C_3 respectively represented the calcination temperature: 400°C, 450°C, 500°C; D_1, D_2, D_3 respectively represented the calcination time: 1h, 2h, 3h.

By means of the orthogonal experiment design and range analyses, the relationship of desulfurization efficiency more than 60% with the desulfurization time were analyzed in Table 2.

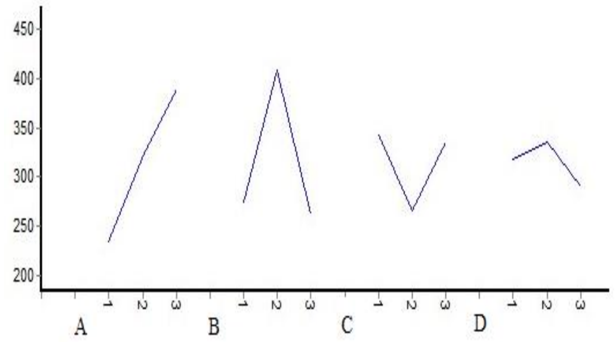
We can see from Table 2, K_1, K_2, K_3 reflected the effect of various factor on the test index, because the high value of the test index was better in this experiment, and $K_{A1}<K_{A2}<K_{A3}$, so you can judge that the A_3 was the optimal level of factor. Similarly, you can determine that B_2、C_1、D_2 were the optimal level of factor B, C, and D separately.

In Table 2, Ri stand for the rang analyses of i column factor, reflected when the level fluctuations of i column factor, the range ability of test indicators .The high value Ri indicated that the factor has more influence on test index, therefore, the factor was more important. The range analyses results listed in Table 2, due to the $R_A>R_B>R_C>R_D$, so you can judge A was the major influence factors on the test index, and then followed by B, C, D.

Table 2. The effects of different factors on the desulfurization efficiency

analyze project	mixing proportion（A）	acetic-acid content（B）	calcination temperature（C）	calcination time（D）	the time of desulfurization efficiency more than 60%/s
1	1	1	1	1	224
2	1	2	2	2	300
3	1	3	3	3	178
4	2	1	2	3	208
5	2	2	3	1	439
6	2	3	1	2	316
7	3	1	3	2	392
8	3	2	1	3	486
9	3	3	2	1	291
K_1	702	824	1026	954	
K_2	963	1225	799	1008	
K_3	1169	785	1009	872	
$\overline{K}_1$	234.00	274.68	342.00	318.00	
$\overline{K}_2$	321.00	408.33	266.33	336.00	
$\overline{K}_3$	389.68	261.68	336.33	290.68	
R_i	155.68	146.65	75.67	45.32	

In order to reflect the laws and trends that impact on the test indexes intuitively, by the factor levels as abscissa, the average of the test index as the ordinate, draw the factors and test index trend in Fig. 3. The figure can be more intuitive to illustrate the change trend of test index with factor levels, indicated the direction for further selective level factors.



A: the mass ratio of activated carbon to diatomite; B: content of acetic acid, C:calcination temperature; D: calcination time

Fig. 3. The effects of the different factors on desulfurization efficiency

3.3 The influence of different preparation factors on the sulfur capacity

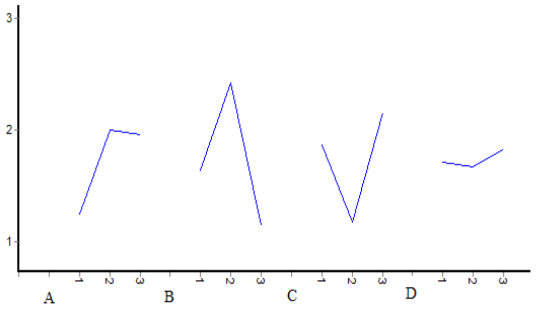
Fig. 4 shown the relationship of different factors with the sulfur capacity, plotted by the average of the test index on the horizontal axis and different factors on the vertical coordinates.

Table 3 was orthogonal experiment design based on penetrating sulfur capacity as single index and the range analyses results, the calculation of penetrating sulfur capacity can be based on: $F=C\times T\times 1000\times 64.06/(22.4\times V)$. The formula: F-penetration capacity of SO_2, mg/ml; C-the volume fraction of SO_2 in the gas, %; T - Breakthrough time, min; 1000 - the gas flow, ml/min; 64.06 - the quality of the SO_2 per mole, mg; V - composite carrier volume, ml; 22.4 - per mole volume of SO_2 gas ml[6].

Table 3. The effects of different factors on the sulfur capacity

analyze project	mixing proportion （A）	acetic-acid content （B）	calcination temperature （C）	calcination time （D）	sulfur capacity
1	1	1	1	1	1.253
2	1	2	2	2	1.302
3	1	3	3	3	1.170
4	2	1	2	3	1.439
5	2	2	3	1	3.089
6	2	3	1	2	1.471
7	3	1	3	2	2.217
8	3	2	1	3	2.873
9	3	3	2	1	0.782
K_1	3.725	4.909	5.597	5.124	
K_2	5.999	7.264	3.523	4.990	
K_3	5.872	3.432	6.476	5.482	
$\bar{K}_1$	1.242	1.636	1.866	1.708	
$\bar{K}_2$	2.000	2.421	1.174	1.663	
$\bar{K}_3$	1.957	1.141	2.159	1.827	
R_i	0.758	1.280	0.985	0.164	

Because the bigger test index was better in this experiment, according to the Table 3 and Fig. 4 can be an analyzed that A_2、B_2、C_3、D_3 were the optimum level of factors A、B、C、D separately. We can seen from the results of range analyses, $R_B>R_C>R_A>R_D$ so B could be determined the major influence factor, and then was followed by C, A and D factors.



A:the mass ratio of activated carbon to diatomite; B: content of acetic acid, C:calcination temperature, D: calcination time

Fig. 4. The effects of the different factors on the sulfur capacity

3.4 The influence of different preparation factors on the specific surface area

Selected four group composite carrier from the orthogonal experiment did the pore structure analysis, one of them 3th sample was a poor group for the desulfurization efficiency while 5th, 7th, 8th samples shown good desulfurization efficiency. The pore structure parameters of four-group composite carrier were shown in Table 4.

Table 4. The pore structure parameter analysis of the composite carrier

Sample	specific surface area m^2/g	Pore area m^2/g	The entrance cm^3/g	Total entrance cm^3/g	The average pore diameter/nm	desulfurization time（more than60%）
3 sample	15.3745	2.3728	0.000908	0.034497	89.7519	178
5 sample	13.7785	1.5019	0.000498	0.037121	107.7660	439
7 sample	13.7529	1.9238	0.000714	0.036453	106.0229	392
8 sample	17.9234	3.6707	0.001484	0.038738	86.4518	486

It can be seen from Table 4 that specific surface area of four compound carriers were between 10 to 20 m^2/g, and far below the specific surface area of activated carbon. The specific surface area of diatomaceous was only between several to dozens, [7] the specific surface area of compound carrier was close to the specific surface area of diatomite. It can be seen that the larger total pore volume the better desulfurization efficiency by comparing the total pole volume with the desulfurization time (more than 60% of the desulfurization efficiency). 8th samples has the best desulfurization performance, while it has the smallest pore diameter and the biggest total pore volume, so 8th sample has abundant number of pores .We could inferred that desulfurization performance of compound carrier was not relative to the specific surface area, but has a lot to do with the pore richness and pore capacity [8-9].

3.5 The influence of different preparation conditions to the pore structure

The pore size distribution results of four composite carriers were shown in Fig. 5. Abscissa shown the bore diameter (nm) and ordinate shown the pore volume (ml/g) in figure.

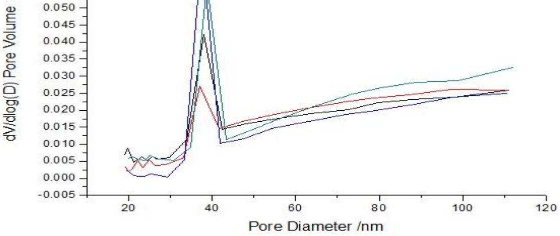


Fig. 5. The result analysis of pore size distribution

The smaller than 2nm called microspore; known as the big hole when bore diameter greater than 50nm; the bore diameter between 2~50nm called mesoporous [9]. It shown that from the result of the analysis. The most proportion of the pore volume was the bore diameter of composite carrier in about 40nm.

Combined with Table 4, it can be seen that with the increasing of pore volume, the desulfurization efficiency of compound carrier also will increased. Therefore, it can be concluded that the quantity of porous has close relationship with the desulfurization efficiency.

4. Conclusion

(1) Desulfurization performance of composite carrier was relative to its preparation technology conditions. It has effect of different mixing ratio of activated carbon to diatomite、acetic acid content、calculation temperature and calculation time on desulfurization efficiency and sulfur capacity. The mixing proportion of diatomite and activated carbon and acetic acid content have a major influence on desulfurization efficiency of composite carrier; acetic acid content and calcination temperature have a main effect on the penetrating sulfur capacity of the composite carrier.

(2) The best preparing condition was shown as follow: the ratio of activated carbon to diatomite 3:2, acetic acid 3ml/10g composite carrier, calcination temperature 400°C, calcination time 3 h.

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