Journal of Iron and Steel Research, International 24 (2017) 979−984

Contents lists available at ScienceDirect

Journal of Iron and Steel Research, International

journal homepage: www.chinamet.cn

Sintering flue gas desulfurization with different carbon materials modified by microwave irradiation

Shan Ren*, Fu-qiang Guo, Qi Zhao, Jie Yang, Lu Yao, Ming Kong
College of Materials Science and Engineering, Chongqing University, Chongqing 400044, China

ARTICLE INFO

Key words:
Microwave modification
Carbon material
Sintering flue gas
Desulfurization

ABSTRACT

Modification of metallurgical coke, biomass char and semi-coke was carried out using a microwave device with power of 450−850 W and irradiation time of 6−12 min. The desulfurization rates of three carbon materials before and after modification were tested. The effects of microwave power and irradiation time on the pore texture and surface chemical characteristics of the three carbon materials were examined by SEM, BET and Fourier transform infrared spectroscopy (FTIR). The results showed that the specific surface area, total pore volume and pore diameter of biomass char and semi-coke after irradiation decreased slightly. Noteworthily, the pore diameter turned small and the acidic functional groups on their surface decomposed, thereby the basicity of carbon surface increased by microwave modification. The optimal promotion of desulfurization rate of three carbon materials was semi-coke irradiated at 850 W for 9 min and the sulfur dioxide adsorption rate was up to 45%.

1. Introduction

With the increase of steel production and the consciousness of environmental protection, iron and steel enterprises are admired to pay more attention to the pollutants handling, especially for sintering flue gas mainly containing SO_2 and NO_x[1-4]. Traditional method for desulfurization of flue gas is the reaction of calcium based compound with SO_2 to generate gypsum. Though the desulfurization method is simple and mature, its vast demand of water, large secondary pollutants and high desulfurization cost make it hard to be an ideal desulfurization method[5-7]. Therefore, in recent years, a lot of researches for better desulfurization methods have been carried out and some advanced techniques have been developed. Among them, dry desulfurization with carbon materials is a good method due to its sustainability and environmental protection effect[2,8-10]. However, the common carbon materials, such as metallurgical coke, biomass char and semi-coke, contain less pore structure and cannot meet the needs of desulfurization efficiency[11-13]. Therefore, improving the pore structure of common carbon materials is needful. In recent decades, many studies have been devoted to carbon materials modification for SO_2 removal from flue gas[8,14-18]. However, most of the studies focused on activated carbon or carbon nano tube (CNT) which was expensive for desulfurization of flue gas in the steel plants. The cheap carbon materials like metallurgical coke, biomass char or semi-coke, on appropriate modification for improving the desulfurization rate, would show large economic advantages.

In this contribution, metallurgical coke, biomass char and semi-coke were modified by microwave irradiation and their desulfurization characteristics were investigated. Besides, desulfurization data were also systematically analyzed and discussed in order to find a suitable carbon material and modification method for sintering flue gas desulfurization.

2. Experimental

2.1. Materials

In this experiment, metallurgical coke was obtained from Xinjiang Bayi Iron & Steel Plant (Xingjiang, China). Biomass char was made from peanut shell, which was dried at 110 ℃ for 10 h and followed by calcination in N_2 at 750 ℃ for 1.5 h. Then, the biomass char was washed with distilled water for removing surface impurities before it was dried at 110 ℃ for

* Corresponding author. Ph.D.
E-mail address: *shan.ren@cqu.edu.cn* (S. Ren).

Received 11 November 2016; Received in revised form 19 January 2017; Accepted 31 January 2017
Available online 15 October 2017

10 h. Semi-coke was from Hami area (Xinjiang, China). Then, the three raw materials were ground and sieved into granules ranging of 1.7－4.0 mm. After being washed with distilled water for 5 times, these carbon materials were dried at 110 ℃ in N_2 for 5 h. For microwave modification experiments, the carbon materials were irradiated at a specific power and a certain time (shown in Table 1), respectively.

Three key factors, the carbon material type, the microwave irradiation power and the irradiation time, were selected and L9 (3^4) orthogonal table design was used in this experiment according to the Taguchi experimental design[19]. Each factor was set to three levels based on the previous studies[17,20]. Details of experimental conditions are presented in Table 1.

Table 1
Orthogonal experimental design of microwave irradiation experiments

Sample No.	Material	Irradiation power/W	Irradiation time/min
M-1	Metallurgical coke	450	6
M-2	Metallurgical coke	650	9
M-3	Metallurgical coke	850	12
M-4	Biomass char	450	9
M-5	Biomass char	650	12
M-6	Biomass char	850	6
M-7	Semi-coke	450	12
M-8	Semi-coke	650	6
M-9	Semi-coke	850	9

2.2. Apparatus

The diagram of the experimental apparatus is shown in Fig. 1. This device mainly included the gas metering and mixing section, reactor and analyzer sections. The gas mixing section consisted of four gas circuits, which were H_2O, O_2, N_2 and SO_2. The maximum flow rates of H_2O, O_2 and SO_2 were 200 mL/min, while the maximum flow rate of N_2 was 1000 mL/min. The highest temperature of the reactor could reach up to 800 ℃. The microwave generator used in this study was NJL2-2 (Nanjing Jiequan Microwave Development Co., Ltd., China), and its working frequency and maximum output power were 2.45 GHz and 1100 W, respectively. The concentrations of gases (NO, NO_x and O_2) were monitored by flue gas analyzer (MRU, Germany OPTIMA7).

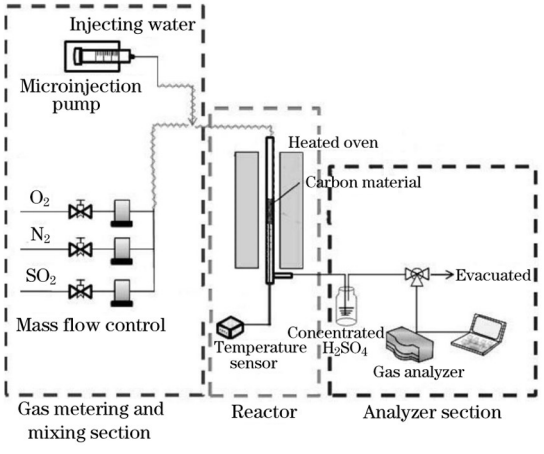

Fig. 1. Diagram of desulfurization tests.

2.3. Experimental method

The desulfurization experiments were carried out in a fixed-bed continuous flow quartz reactor (10 mm of internal diameter) at 150 ℃. In each experiment, 2 g sample was loaded and the reactor was heated by a temperature-controlled furnace. The feed gas contained 0.126% SO_2, 11% O_2, 7.5% H_2O and N_2 as balance. The total gas flow rate was 200 mL/min. The concentration of SO_2 at the reactor outlet was recorded by OPTIMA7. The high purity nitrogen was added as a protect gas before reaching the target temperature. The reaction gases were injected after the temperature remained at 150 ℃ for 30 min. SO_2 conversion was calculated as follows:

$$DS=\left(1-\frac{\alpha}{\beta}\right)\times 100\% \quad (1)$$

where, DS is the desulfurization rate, %; α is the SO_2 concentration at the reactor inlet; and β is the SO_2 concentration at the reactor outlet.

The structures, surface properties and surface chemical compositions of carbon materials before and after modification were investigated using BET (the surface area, total pore volume and average pore size were measured by N_2 adsorption at 77 K using Micromeritics 3H-2000PS1), SEM (FEI Nova 400) and FT-IR (Nicolet, iS5).

3. Results and Discussion

3.1. BET and SEM results

The surface area, pore volume and pore diameter of different samples are given in Table 2. From the table, the specific surface area of metallurgical coke increased remarkably but there was nearly no change

Table 2
BET results of carbon materials before and after modification

Sample	Specific surface area/ ($m^2 \cdot g^{-1}$)	Total pore volume/ ($cm^3 \cdot g^{-1}$)	Average pore size/ nm
Metallurgical coke	0.6205	0.0001	1.3001
M-3	1.7281	0.0001	1.4740
Biomass char	434.9443	0.2085	0.6878
M-6	262.5894	0.1215	0.6590
Semi-coke	35.7790	0.0141	0.8105
M-9	25.6324	0.0103	0.7923