Fuel Processing Technology 148 (2016) 35–42

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Research article

Effect of microwave irradiation on the preparation of iron oxide/arenaceous clay sorbent for hot coal gas desulfurization

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ARTICLE INFO

Article history:
Received 25 July 2015
Received in revised form 12 January 2016
Accepted 31 January 2016
Available online xxxx

Keywords:
Iron oxide sorbent
Arenaceous clay
Microwave irradiation
Conventional heating
Hot coal gas desulfurization

ABSTRACT

For applications in the high temperature coal gas desulfurization process, iron oxide/arenaceous clay sorbents were prepared by microwave irradiation and conventional heating, respectively. The desulfurization performances of sorbents were evaluated using a fixed-bed reactor with simulated coal gas. The effects of calcination temperature and microwave heating time on the properties of sorbents were also investigated. The microwave-irradiated sorbents exhibit sulfur capacity and reactivity greater than those prepared by conventional heating. X-ray diffraction, X-ray photoelectron spectroscopy, a scanning electron microscope, a transmission electron microscope and N_2 adsorption were used to characterize the physical and structural properties of the sorbents. Several benefits have been observed using microwave heating rather than conventional heating for the preparation of sorbents. The results indicate that microwave irradiation leads to better inner structure of sorbent and more uniform distribution of the active component with smaller particle size, which facilitate chemical reaction and mass transfer. Microwave irradiation also results in greater outer layer electron density and higher contents of surface metal element, both of which are beneficial to the increase of absorption efficiency and desulfurization reactivity. Then the microwave-irradiated sorbents were tested for three successive sulfurization–regeneration cycles, the 3rd regenerated sorbent still performed well with no apparent deterioration, it proved that the sorbent has good regenerability and is suitable for hot gas desulfurization.

1. Introduction

Sulfur compounds, especially H_2S and COS, are the major impurities in coal-derived synthesis gas [1,2]. These sulfur species must be removed from syngas prior to its utilization due to their negative effects on chemical processing steps and the environment. As an efficient way for H_2S removal at high temperatures, several studies have focused on the development of non-catalytic gas–solid reactions between H_2S and appropriate metal oxide sorbents [1,3]. It has been shown in the pioneering work of Westmoreland and Harrison that the thermodynamics of H_2S sorption on various metal oxides are extremely favorable [3]. In particular, sorbents based on iron oxide (Fe_2O_3) have been the focus of special research interest as durable high-temperature desulfurizers due to their attractive properties such as high sulfur capture capacity and excellent regeneration capability. In addition, iron oxides are inexpensive and abundant compared with the other metal oxides [4–8].

During the sulfidation process of iron oxide, oxygen atoms are replaced by the larger sulfur atoms, which leads to a decrease in the pore volume and thus there is the potential for inner pores to get plugged, consequently, the mass transportation and gas diffusion will be restrained in the sulfidation process [8–10]. Previous studies have demonstrated that the desulfurization performance could be substantially improved if the active species could be distributed with a high level of dispersion on a sufficient porous texture of the sorbent [11,12]. Therefore, in this work, Fe_2O_3 was obtained by the thermal decomposition of $FeC_2O_4 \cdot 2H_2O$, which resulted in a large amount of CO and CO_2 gases being released. The gas evolution was found to be extremely favorable for the formation of a porous structure [12].

In order to improve the desulfurization performance, binders such as kaolinite, have been added into sorbents [13]. A previous study showed that by adding a bentonite binder into zinc ferrite, the resulting sorbent pellets became more durable and more dense and possessed much greater mechanical strength [14]. The previous work reported by Fan et al. indicated that the addition of a clay binder influenced both the sulfur capacity and the stability of the resulting sorbent. The clay binder was found to be responsible for forming the texture of the sorbent during the calcination process [12]. Based on these results, arenaceous clay was used as an inorganic binder in this study to improve the desulfurization performance.

Compared with the conventional heating process, which is time-consuming [15], microwave heating has shown to dramatically reduce reaction times and increase product yields [15,16]. Microwave heating of materials causes rotation of the dipole moments of molecules, and the energy absorbed is dissipated as heat within the material. Microwave heating is therefore an internal process as compared to conventional

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http://dx.doi.org/10.1016/j.fuproc.2016.01.037
0378-3820/

heating which is external [17]. Another unique feature of microwave heating is related to the athermal-non-Arrhenius effect, in which there is a reduction of activation energy or an increase in the pre-exponential factor for chemical reactions [18–20]. In our previous work, it was found that the microwave heating method resulted in better quality sorbents due to improved structures [21]. Microwave heating is also environment-friendly, simple to operate and energy efficient compared to the conventional heating methods [22,23].

In this paper, we reported the syntheses of desulfurizers prepared by microwave and conventional heating and their desulfurization performances have been evaluated and compared. Meanwhile, the sulfidation–regeneration tests were evaluated to investigate regeneration ability for the reuse of the sorbent. The work can be particularly valuable for the sorbent development for fixed-bed reactors as well as other applications, where sorbent performance is crucial.

2. Experimental

2.1. Preparation

$FeC_2O_4 \cdot 2H_2O$, the precursor of Fe_2O_3, was prepared by a solid-state method with $FeCl_2 \cdot 4H_2O$ and $H_2C_2O_4 \cdot 2H_2O$ (AC grade) as the raw materials. The starting materials were weighed and mixed thoroughly at a molar ratio of 1:1 and finely homogenized in an agate mortar before oven-drying for 1 h. Finally, the mixture was dried in an oven at 80 °C for 2 h for complete removal of water. Iron oxide sorbents were prepared from the mixture of $FeC_2O_4 \cdot 2H_2O$ and arenaceous clay binder (SiO_2:Al_2O_3:Fe_2O_3:TiO_2:Others = 61.59:19.62:10.49:3.2:5.1). The mixture was crushed and homogenized in a ball mill for 2 h. Then, water was added to the powdered mixture in order to achieve a thick paste with the appropriate consistency to be extruded using a syringe. The sorbent was extruded in a cylindrical shape with a 3 mm diameter and 3 mm height, and then oven-dried at 90 °C for 3 h. Finally, the sorbents were calcined with a heating rate of 5 °C/min with different target temperatures for different lengths of time by separate microwave heating and conventional heating processes. Preparation methods and compositions of sorbents calcined at 500 °C were shown in Table 1, respectively.

2.2. Desulfurization and regeneration evaluations

Desulfurization and regeneration performances were conducted in a quartz fixed-bed reactor (17 mm in inner diameter, 650 mm in length), equipped with mass flow controllers. A type-K thermocouple was placed in the middle of the sorbents to monitor the sample temperature. Analyses of the outlet and inlet gas from the reactor were carried out by gas chromatography using a thermal conductivity detector and a flame photometric detector for detection of H_2S. Desulfurization evaluations were carried out at 500 °C on the fresh and regenerated sorbents, 10 g of sorbent was used in each experiment, passing a flow rate of 333 ml/min. The composition of the simulated coal gas stream is H_2S (2500 ppm), CO (27%), H_2 (39%), CO_2 (12%), and N_2 (balance gas). The desulfurization evaluations, through the respective breakthrough curves plotted versus the breakthrough time *t*, ended when the H_2S concentration in the outlet gas from the reactor was higher than 500 ppmv. The sulfur capacity (SC) of sorbent was calculated by following equation:

$$\mathrm{SC} = \mathrm{WHSV} \times \frac{\mathrm{M_S}}{\mathrm{V_m}} \times \int_0^t (C_{in} - C_{out}) dt \times 10^{-4}.$$

WHSV is the weight hourly space velocity ($\mathrm{L\,h^{-1}\,g^{-1}}$); M_S stands for the molar weight of S (32.06 g $\mathrm{mol^{-1}}$); V_M is the molar volume of H_2S at 1 atm and 25 °C (24.5 L $\mathrm{mol^{-1}}$), and *t* is the breakthrough time of the desulfurization process. After desulfurization, the regeneration of FA-3 was performed with a gas mixture (2 vol.% O_2, N_2 balance) at the temperature of 650 °C. 10 g of sulfided FA-3 was used in regeneration and the gas flow rate is 333 ml/min. The high purity nitrogen was added before the temperature was up to target temperature working as a protect gas and the reaction gas was injected at the temperature of 650 °C. Iodometry was used to periodically detect the concentration of SO_2 in outlet gas, and the regeneration was considered to be complete when SO_2 was not traced in the outlet gas from the reactor.

2.3. Characterization

The crystal structure and morphology of the sorbents were analyzed by SEM (JSM-26360LV). The phases of the sorbents before and after desulfurization were characterized by powder XRD using an X-ray diffractometer (Rigaku D/max-2500, Japan) with monochromatized Cu Kα radiation, a scan range from 5° to 80° at a scanning speed of 8°/min, and a power setting of 40 kV. The average crystal size corresponding to the calcination temperatures were estimated using Scherrer's formula as shown below [24]:

$$\mathrm{D} = \frac{0.89\lambda}{\beta \cos(2\theta)} \tag{2}$$

where λ is the X-ray wavelength of Cu Kα radiation source (=0.15418 nm), β is the full width at half maximum intensity of the diffraction peak, and θ is the Bragg angle.

The specific surface areas and the pore size of the sorbents before and after sulfurization and regeneration were determined by nitrogen adsorption and desorption using a BET instrument (Micromeritics TriStar-3000). The XPS patterns were obtained with a PHI5000C spectrometer using an Al Kα source operating at 250 W and 93.9 eV pass energy. Energy calibration was done by using the C 1s peak at 284.6 eV.

The content of sulfur in the sorbent was measured by a KZDL-8F-type fast-smart sulfur instrument made by Hebi Xianke Coal Instrument Co., Ltd. In the characterization, the sorbent (0.1 g) was combusted under the high temperature of 1150 °C and all forms of sulfur in the sorbent were decomposed and oxidized as SO_2 and then combined with water to form H_2SO_3. According to the coulomb titration, the return to the dynamic balance of the original amount of current consumptionis directly related to the amount of decomposition of sulfur in the sorbent. It can be measured and calculated by the microprocessor and we can get the total sulfur content in sorbent.

3. Results and discussion

3.1. Effect of active component content

The desulfurization performances of the sorbents with different amounts of the active components were evaluated at 500 °C. As shown in Fig. 1, the sorbent named FA-3 showed the highest H_2S removal efficiency and the longest breakthrough time among the four candidates, with a total pre-breakthrough time of approximately 15 h, corresponding to an effective sulfur capacity nearly 9.88 g S/100 g sorbent. In the sulfidation process, sulfur capacity and desulfurization reactivity generally show a linear relationship with the content of active

Table 1
Preparation methods and compositions of sorbents calcined at 500 °C.

Sorbent	Heating method	Heating temp (°C)	Heating time (min)	Fe_2O_3 (wt%)	Supporter (wt%)
FA-1	Microwave	500	30	20	80
FA-2	Microwave	500	30	25	75
FA-3	Microwave	500	30	30	70
FA-4	Microwave	500	30	35	65
CFA-3	Conventional	500	30	30	70