Fuel 203 (2017) 233–243

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

Insights to the microwave effect in the preparation of sorbent for H_2S removal: Desulfurization kinetics and characterization

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HIGHLIGHTS

- Microwave was applied to prepare sorbents used for syngas desulfurization.
- Iron oxide sorbents were prepared by microwave and conventional heating.
- Microwaves lead to more porous structure and raise the surface area of sorbent.
- Desulfurization performance of sorbent can be improved through microwave heating.

ARTICLE INFO

Article history:
Received 23 December 2016
Received in revised form 7 April 2017
Accepted 24 April 2017
Available online 3 May 2017

Keywords:
Sorbent preparation
Microwave heating
H_2S removal
Desulfurization kinetics
Adsorption efficiency

ABSTRACT

High temperature coal gas desulfurization is an efficient and environmental-friendly process for clean coal technologies such as the integrated coal gasification combined cycle. This study adopted microwaves as the energy source to prepare iron oxide desulfurization sorbents and investigated the effect of microwave heating on the properties of the sorbents. The desulfurization kinetics of H_2S removal by the two kinds of sorbents heated using both microwave and conventional method were studied and the sorbents were characterized by means of X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), N_2-adsorption and energy dispersive spectrometry (EDS). The shrinking core model was used to describe the desulfurization reaction. The calculated activation energies of microwave-heated sorbent in the regions of chemical reaction and diffusion control were both smaller than those of the conventional-heated sorbent. The characterization data indicate that the sorbents prepared by microwave heating have higher contents of active metal elements on the surface, which improve the adsorption efficiency. Fractal dimensions were calculated based on Frenkel-Halsey-Hill theory and the results revealed that the fractal dimension of microwave-heated sorbent is 2.850 and that of conventional-heated sorbent is 2.832. The results indicate that microwave irradiation provides a more porous internal structure and irregular surface which facilitates gas transfer during the desulfurization process. Overall, the microwave heating method produced sorbents with better H_2S removal performance, suggesting the potential of using this method to prepare improved industrial sorbents.

1. Introduction

The rapidly increasing energy demands are likely to exhaust the global energy reserves and generate serious global climate deterioration unless suitable solutions are implemented. Thus, there is an urgent need to develop environmentally-friendly, energy efficient systems. The Integrated Gasification Combined Cycles (IGCC) energy generation system and Fischer-Tropsch based processes, such as coal, biomass, or gas to liquid methods, represent alternative energy production technologies that are efficient and cleaner [1–4]. Gasification of feeds into a synthesis gas is the fundamental first step in both technologies. In IGCC, the electricity is produced by a gas turbine through burning of syngas. In the Fischer-Tropsch based reactions, the syngas transforms into ultra-clean liquid hydrocarbon based fuel. Moreover, syngas could be employed to produce heat and energy sources such as natural gas and liquid fuels. However, a significant problem in using the synthesis gas is the presence of sulfur containing contaminants [5,6], such as H_2S and small amounts of COS and CS_2, which need to be almost entirely removed at high temperature to achieve the optimum thermal efficiency of generation system and avoid downstream process equipment corrosion and catalyst poisoning [7]. A thorough desulfurization is necessary to meet the strict sulfur

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http://dx.doi.org/10.1016/j.fuel.2017.04.095
0016-2361/

tolerance standards for important applications [4,8]. In order to solve this problem, several researchers have made efforts in the development of a highly efficient hot gas desulfurization (HGD) process. In comparison to the conventional wet desulfurization technology, HGD has the advantage of effectively removing H_2S without much heat loss or the requirement for wastewater treatment [4]. As an efficient method for the removal of H_2S, researches have focused on hot gas desulfurization based on the reactions between hydrogen sulfide and metal oxide sorbents. According to the detailed operating conditions and tolerance limit of sulfur, appropriate metal oxides can be selected for the desulfurization reaction by investigating sulfur removal capabilities of potential metal oxides [4,9]. The effectiveness of this process depends upon the development of sorbent with good desulfurization performance, excellent structural stability in cyclic process, regeneration ability, and thermal stability [6]. Among the metal oxide sorbents, iron oxide sorbent has been used frequently for this purpose due to its high sulfur capacity and excellent performance after regeneration [10]. Moreover, iron oxides are abundant in nature compared to other sorbents.

A common consensus is that there is a positive correlation between desulfurization reactivity and the available sorbent surface area and pore volume. The structural sintering of sorbent during high temperature calcination and desulfurization causes the reduction of specific surface area and the accompanying loss of reactivity. During the desulfurization process, the pore volume and surface area are reduced and thus there is the potential for the internal pores to get blocked. Consequently, the mass transfer and diffusion will be limited due to the replacement of oxygen atoms by the sulfur atoms with larger molecular volume [11,12]. Many scholars have argued that the desulfurization efficiency will be largely promoted if the active species could be uniformly dispersed on an ample porous structure of sorbent [13]. An improved capacity of H_2S removal was found for ZnO sorbent by Samokhvalov and Tatarchuk due to the high surface area of the porous material. The authors showed that the yield and desulfurization efficiency of ZnO sorbent with high surface area were better compared to a commercial ZnO as H_2S desulfurizer [14]. They also noted that not only the pore structure but also the microstructure of the grain are crucial to optimize the nanostructure with larger pore sizes. Gupta et al. studied multiple desulfurization-regeneration cycles with zinc ferrite sorbents, and suggested that the loss in reactivity was likely caused by the deterioration in chemical and structural properties as well as the wearing down of sorbent caused by abrasion [4,15]. In order to solve the problems related to the loss in reactivity caused by structural deterioration, high surface area materials such as SBA-15 [7], MCM-48 [16], CNT [17] and MOF [18] have been applied in the preparation of desulfurization sorbents by many scholars. However, the high costs of the above materials have extremely limited their further industrialization as desulfurization sorbents.

Over the years, microwave processing has been frequently employed in the preparation of activated carbon [19–21], pyrolysis of biomass or waste [22,23], and processing of various sorbents [24–26] due to its advantages such as (a) heating without contact; (b) selective heating; (c) fast heating; (d); volumetric heating; (e) increased flexibility to start and stop arbitrarily; (f) higher product yield; (g) time-saving; and (h) orientated or tailored material surface and structure properties [27]. A recent study performed a theoretical calculation about energy-savings within an endothermic reaction using microwave and conventional heating as heat source and showed the reduction of energy consumption when microwave heating was used [28]. They suggested that microwave-metal discharge can be employed in a series of engineering fields. Many efforts also focus on using microwave heating to improve the yield and quality of products and eradicate the formation of undesired by-products [27]. Different from conventional methods, microwave heating shows the ability to improve product quality, and avoid deterioration of product strength and surface properties induced by high temperatures sintering [27]. Microwaves can inhibit the grain growth and produce samples with more uniform grain distribution throughout the sample [29]. Moreover, microwave heating also prevents the aggregation of materials, resulting in better mechanical properties in comparison to conventional-heated materials [29,30]. It has also been found that microwaves have the ability to significantly increase the diffusivity of ions compared to conventional heating. Wu et al. [29] reported that the surface concentrations of Zn^{2+} and O^{2-} on the surface of microwave-heated desulfurizer were nearly two times greater than those of conventional muffle heated desulfurizer, indicating that microwaves can effectively promote the diffusion of ions from the interior to the surface of the desulfurizer and thus benefit the desulfurization reaction. Similar behavior was also reported by Qi et al. [31].

The fractal theory was introduced by Mandelbrot and first applied to describe the complexity of porous media by Avnir and Pfeifer [32–34]. With the development of research, the fractal theory is found to be a useful tool for characterizing the structure and morphology properties of a sample [35]. Fractal dimension is an intrinsic characteristic of the surface and it reflects the roughness of structure. For a fractal material, the factors such as surface area and pore size distribution contribute to the fractal dimension. Thus, the fractal dimension is a comprehensive description of the surface roughness and irregularities [36]. The value of fractal dimension lies between 2 and 3, and these two boundary values represent a perfectly smooth surface and extremely irregular surface, respectively [36]. Fractal dimensions can be obtained from small-angle X-ray scattering (SAXS), micrographs, small angle neutron scattering (SANS) and gas adsorption [37]. Among these methods, gas adsorption is widely used to analyze the fractal features of a surface. The Frenkel-Halsey-Hill (FHH) model describing multilayer adsorption coverage is an important type of adsorption method and is frequently used to measure the fractal dimensions due to its convenience and applicability. The FHH model only requires one adsorption isotherm to easily determine the fractal dimensions [38].

The present work focuses on the application of microwave technique in the preparation of desulfurization sorbents and provides a detailed analysis on the improved properties of desulfurization sorbents prepared via microwave heating compared to conventional heated sorbents. The surface and structural characteristics of the two kinds of sorbents were characterized by means of XRD, XPS, N_2 adsorption, SEM-EDS, and elemental-mapping studies. The experimental results were compared with the theoretically calculated results to obtain a comprehensive understanding of the effects of microwave on the properties of the sorbent.

2. Experimental

2.1. Preparation of sorbents

The detailed preparation conditions of the sorbents were reported in our previous study [30]. The physical properties of the sorbents prepared by microwave (MW) and conventional heating (CH) are given in Table 1. In the lab-made microwave heating system (patent-pending), a quartz tube was inserted in the microwave tube furnace (manufactured by Qingdao MKW Microwave Applied Technology Co., rated power of furnace is 2.4 kW), and the temperature of the sorbent bed in the middle of quartz tube was measured using a special thermocouple placed inside the reactor and controlled based on PID (Proportional-Integral-Differential)