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Effect of temperature-programmed pyrolysis pre-treatment on desulfurization performance of Zn-based sorbent prepared by lignite as support

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ABSTRACT

A series of Zn-based sorbents were prepared by high-pressure impregnation with lignite as precursor of support and zinc nitrate as the precursor of active component, followed by temperature-programmed pyrolysis of the impregnated lignite sample in a fixed-bed quartz reactor. The H_2S removal performances of sorbents prepared under different pyrolysis conditions such as temperatures, holding time as well as heating rates were evaluated. The physical and chemical properties of sorbents were characterized by atomic absorption spectroscopy (AAS), X-ray diffraction (XRD), transmission electron microscope (TEM) and nitrogen adsorption techniques. The results show that the process of pyrolysis can improve the pore structure dramatically, which lead to the high specific surface area and large pore volume. The good desulfurization performance of sorbent was attributed to both of the proper porous structure of sorbents, the content and distribution of active component. The optimal operating conditions of temperature-programmed pyrolysis for the impregnated lignite sample were the heating rate of 10 °C/min, holding time of 180 min in N_2 atmosphere and pyrolysis temperature of 550 °C. The sulfidation time could hold for over 720 min before reaching 1 ppm H_2S in outlet gases and the sulfur capacity was up to 25.91 g S/100 g ZnO for sorbent prepared under this optimized condition.

1. Introduction

Coal gasification is now the foremost technology of coal chemical industry, and it still holds a central position in the foreseeable future. But about 80% of sulfur containing in coal will be converted into S-containing gases in the process of coal gasification (Xie et al., 2006). It is one of issues that must be focused on for the successfully accomplishing of this technology. H_2S, accounting for approximate 90% of sulfur species in coal gases (Qiu et al., 2011), is necessary to be removed, not only because of its oxidation products acting as the major source of the acid rain (Zhang et al., 2010; ter Maat et al., 2005), but also its negative impact on industry application by corroding pipeline and poisoning catalysts (Rosso et al., 2003; Cheah et al., 2009).

Currently, there is a driving force for searching mid-temperature clean process of coal-derived fuel gas to make gasification, gas cleanup and downstream processing be more thermally efficient, more economically viable and environmentally friendly (Mureddu et al., 2012; Meng et al., 2010). Many single metal oxides and mixed oxides sorbents based on iron oxide (Fan et al., 2013), cerium oxide (Mullins and McDonald, 2007), manganese oxide (Jia et al., 2012), calcium oxide (Chauk et al., 2000), zinc ferrite (Ikenaga et al., 2004) and zinc titanate (Pineda et al., 1998) as active component were prepared by various methods. Zinc oxide sorbents have

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attracted more attention because of its favorable thermodynamics, high precision, and stability for the removal of H_2S. At present, one of the most heated topics is for adsorption in the desulfurizing processes on various porous materials, such as activated carbon (Qiu et al., 2011; Seredych and Bandosz, 2008; Adib et al., 2000), modified activated carbon (Bagreev et al., 2004), modified zeolites (Kumar et al., 2011; Maugé et al., 2002), modified clay (Nguyen-Thanh and Bandosz, 2003), γ-Al_2O_3(Zhang et al., 2003; Wang et al., 2013), mesoporous silica (Zhang et al., 2014), semi-coke (Mi et al., 2012a), etc. Semi-coke is obtained from a low-temperature carbonization process of low-rank coal, in which pore structure that might provide a good site for desulfurization, has been developed to some extent (Zheng et al., 2011; Mi et al., 2012b).

Due to high water content, low calorific value, lignite is essential to be upgraded before applied into industry. In addition, low heat utilization rate of lignite combustion, serious environmental pollution and poor adaptability for gasification require us to broaden the effective utilization range of lignite. Because of its abundant pore structure and high water adsorption for oxygen-containing functional groups, lignite is feasibly used as raw material for preparation of semi-coke supported zinc oxide by high-pressure impregnation method. The results in our previous study (Ren et al., 2014) have shown that hydrothermal synthesis of sorbent through high-pressure impregnation of the active component precursor on the semi-coke support can simultaneously improve its pore structure and the impregnation conditions for sorbent preparation have been optimized. However, different from semi-coke support, a step involving the pyrolysis of lignite and synergistically thermal decomposition of the active component precursor is indispensable when raw lignite was directly used to load active component in zinc nitrate solution. In this process, the structure of support and the dispersion of active component may be improved. So, the effect of temperature-programmed pyrolysis on desulfurization performance of zinc-based sorbents prepared by changing pyrolysis conditions was investigated in this paper.

2. Experimental

2.1. Preparation of Sorbents

Zinc-based sorbents were prepared by the high-pressure impregnation and pyrolysis of impregnated sample. $ZnNO_3{\cdot}6H_2O$ (AR, 99%, Tianjin Kemiou Chemical Reagent Co. Ltd, China) was precursor of active component and lignite was precursor of support. Lignite, its proximate and ultimate analysis results showing in Table 1, was screened to the particle sizes of 2.38–3.36 mm (6–8 mesh) and then dried for 240 min at 80 °C in vacuum oven with the vacuum degree of 720 mm mercury column, then 20 g of dried lignite was added into 34 mL 36 wt% zinc nitrate solution. The mixture was placed in the sealed autoclave and heated in muffle furnace for 300 min at 20 atm, which was conducted by controlling the temperature at 213 °C, followed by cooling to room temperature. The samples were filtered to remove the excess liquid and then dried for 360 min at 80 °C in vacuum oven with the vacuum degree of 720 mm mercury column.

About 30 mL dried samples were placed in constant temperature zone of the fixed-bed quartz reactor (internal diameter 2.0 cm) and heated to specific temperatures (450, 500, 550 and 600 °C) with certain heating rate (5, 10, 12 and 15 °C/min) and maintaining for some time (60, 120, 180, 240 min). A flow rate of 500 mL/min nitrogen atmosphere (99.99%) was adopted in whole process. The prepared sorbent was designated as TxtyRz, where x is the pyrolysis temperature, y is the holding time at x °C, z is the heating rate. And the sulfided sorbent was denoted as TxtyRz-S.

2.2. Characterization of sorbents

The crystalline phase of the sorbent was determined by X-ray diffraction (Rigaku D/max-2500, Japan) with Cu-Kα ($\lambda = 0.15406$ nm) radiation at settings of 40 kV and 100 mA, over a 2θ range of 15–85° using a scan rate of 8°/min. The content of Zn in the sorbent was measured by an atomic absorption spectrum instrument (AA240FS, America) with working lamp current of 2.0 mA, the spectral band width of 0.2 mm and the combustion gas of acetylene-air. The texture properties of the sorbent were measured by Micromeritics ASAP-2000 analyzer (Micromeritics Instrument Corp, America) at 77 K with the isotherms of nitrogen adsorption/desorption. The surface morphology was observed by using a transmission electron microscope (JEM2100F, JEOL, Japan). The specific surface area of the sorbent was assessed by the Brunauer–Emmett–Teller (BET) method. The Barrett–Joyner–Halenda (BJH) model was used to determine the pore size distributions over the mesopore and part of the macropore range. The pore size distributions of micropores were calculated by the Horvath–Kawazoe (HK) model.

2.3. Desulfurization tests of sorbents

The desulfurization tests were conducted in a fixed-bed reactor with 20 mL sorbent placed in a vertical quartz tube at atmospheric pressure and 400 °C. The simulated coal gas was composed of H_2 (39 vol%), CO (33 vol%), CO_2 (19.7 vol%), H_2O steam (1 vol%), H_2S (1000 ppm in volume) and N_2 (balance) with a space velocity of 2000 h^{-1}. Gas chromatography equipped with a flame photometry detector (FPD) was used to determine the inlet and outlet H_2S concentration. The experiment was terminated when outlet H_2S concentration exceeded 20 ppm. In this study, the breakthrough time was defined as the time from the beginning of the desulfurization to the time when the exit H_2S concentration reached 1 ppm. The sulfur capacity is the mass of sulfur adsorbed before breakthrough by 100 g of ZnO. The

Table 1 – Proximate and ultimate analyses of raw lignite.

Proximate analysis (wt%)			Ultimate analysis (wt%, daf)				
M_{ad}	A_{ad}	V_{daf}	C	H	N	S	O*
8.25	5.30	31.49	80.40	4.31	0.93	0.12	14.24

Note: ad is air-dried basis, daf is dry and ash-free basis.

* By difference.