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The mechanism of coal gas desulfurization by iron oxide sorbents

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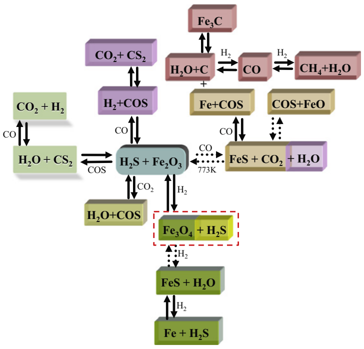
HIGHLIGHTS

- The existence of CO and H_2 affects equilibrium concentrations of H_2S and COS.
- The presence of H_2 has a negative effect on H_2S removal.
- By-products including COS, CS_2, CH_4, and Fe_3C have vital influence on the reaction.
- The pathways of Fe_2O_3 reacting with H_2S were successfully established.
- The major route of the reaction mechanism is Fe_2O_3 reacting with H_2S to form FeS.

GRAPHICAL ABSTRACT



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ABSTRACT

This study aims to understand the roles of hydrogen and carbon monoxide during the desulfurization process in a coal gasification system that H_2S of the syngas was removed by Fe_2O_3/SiO_2 sorbents. The Fe_2O_3/SiO_2 sorbents were prepared by incipient wetness impregnation. Through the breakthrough experiments and Fourier transform infrared spectroscopy analyses, the overall desulfurization mechanism of the Fe_2O_3/SiO_2 sorbents was proposed in this study. The results show that the major reaction route is that Fe_2O_3 reacts with H_2S to form FeS, and the existence of CO and H_2 in the simulated gas significantly affects equilibrium concentrations of H_2S and COS. The formation of COS occurs when the feeding gas is blended with CO and H_2S, or CO_2 and H_2S. The pathways in the formation of products from the desulfurization process by the reaction of Fe_2O_3 with H_2S have been successfully established.

1. Introduction

Integrated Gasification Combined Cycle (IGCC) is one of the most ideal technologies with high power generation efficiency and environmental friendly performance (Song et al., 2013; Fan et al., 2013b). Coal currently is the most abundant fossil fuel with relatively low and constant price. However, reserves of fossil fuels have been limited and global warming crisis is increasing (Monazam et al., 2012). Therefore, the technology improvement for energy issues has become a trend nowadays, especially coal poly-generation with IGCC. Sulfur contained in coal will be emitted to typically form 0.2–3 vol% H_2S and lesser amounts of other sulfur compounds during the process of gasification (Monazam et al., 2012). Long-term exposure to these sulfur-containing species may cause the components of IGCC system severely corrosive damage. Therefore, multiple impurities must be removed to comply with environmental laws and regulations for protecting the public health and reducing maintenance costs. Nowadays, almost all commercial IGCC power plants use wet desulfurization processes to

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remove H_2S and other deleterious gases from hot syngas by the use of large amount of water, resulting in the decreasing thermal efficiency of the system (Lee and Feng, 2012). Consequently, the development of dry desulfurization at high temperature becomes vitally crucial in this field, and can improve the thermal efficiency and reduce cost of capital without the procedure of coal gas cooling and heating (Wan et al., 2011).

Several researchers have reported on the important role of metal sorbents on the performance of hot-gas desulfurization (Jung et al., 2013; Zhang et al., 2013; Fan et al., 2013a). The sorbents can be divided into noble metal sorbents (Ru and Rh) (Hulteberg et al., 2005) and base metal oxide sorbents (Mn, Cu, Fe, Zn) (Li and Flytzani-Stephanopoulos, 1997; Wan et al., 2011; Zhang et al., 2012; Zheng et al., 2012). Iron oxide is the most common material as a sorbent for hot gas desulfurization under a reducing atmosphere with hydrogen and carbon monoxide due to its high absorption capacity, abundant resources, lower price, excellent physical strength and easy regeneration (Wang et al., 2011; Fan et al., 2013a). In our previous study (Tseng et al., 2008), the Fe-based sorbents emerged as the leading candidates for hot coal gas desulfurization through thermodynamic screening. In this study, the influences of CO and H_2 on the performance of 10 wt.% Fe_2O_3/SiO_2 sorbents for H_2S removal were evaluated in various simulated syngas. The syngas (H_2S) before and after the reactor were recorded by a gas chromatograph (Shimadzu, GC-14B) equipped with a flame photometry detector (FPD) and fitted with a GS-Q capillary column. The outlet gases were recorded through on-line Fourier transform infrared (FTIR) spectroscopy and GC-FPD. A further investigation into the desulfurization mechanism of the sorbents was also conducted. The results will provide useful information for the designs and applications of the sorbents in the IGCC system.

2. Experimental

2.1. Sorbent preparation

The Fe_2O_3/SiO_2 sorbents were prepared by incipient wetness impregnation. Commercial SiO_2 spherical pellets (Alfa Aesar, stock #44740) were used as sorbent supports. On the basis of the predetermined contents of iron loading from our previous study Huang (2007) and Bukhtiyarova et al. (2007), 5.63 g ($Fe(NO_3)_3 \cdot 9H_2O$) was used as the precursors of Fe dissolved in 16 mL de-ionized water and then mixed with the 10 g SiO_2 supports. The impregnated materials were kept at room temperature for 12 h to let solution fully penetrate into the pore of supports. Subsequently, the impregnated sorbents were dried in an oven at 393 K for 24 h. Finally, the impregnated sorbents were conducted in a calcination process at 973 K for 8 h in airflow conditions to become 10 wt.% Fe_2O_3/SiO_2 sorbents.

2.2. Sorbent characterization

In the present work, temperature-programmed reduction (TPR) with hydrogen was conducted in a TG/DTA (Pyris Diamond TG/DTA, Perkin Elmer) to determine the phase transformation in the temperature range from room temperature to 1073 K with a heating rate of 50 K min^{-1}. Elemental analyses (EA) were provided with an Elementar Vario EL-III elemental analyzer.

2.3. Desulfurization experiment

The H_2S removal experiments were carried out in a bench-scale fixed-bed reactor (a quartz tube with 1.5 cm id, 1.8 cm od, and 85 cm long) with 10000 ppm inlet H_2S at atmospheric pressure and 773 K. A thin layer of #200 mesh frit quartz disk was set in the reactor 45 cm below the top of the tube to support the catalyst and uniformly distribute the gas stream. The weight of the catalyst packing was 1 g (thickness 0.82 cm). The weight hourly space velocity (WHSV) was set at 2000 mL h^{-1} g^{-1}. 773 K and 2000 mL h^{-1} g^{-1} were chosen because it provided the best performance for H_2S removal according to previous studies (Ko et al., 2006a; Tseng et al., 2008). The experimental apparatus included a simulated syngas system, a high-temperature reaction system, and a gas analysis system.

The simulated syngas had a typical composition of 1 vol% H_2S, 25 vol% CO and/or 15 vol% H_2, and N_2 as a balance gas, supplied from gas cylinders, mixed in a mixer to ensure the gas mixture was well mixed, and then introduced to the reaction system. The high-temperature reaction system was consisted of a bench-scale fixed-bed reactor, an electrical furnace, a temperature controller (TTE, TM-4800), and a K-type thermocouple. The gas analysis system was composed of a GC-FPD and a FTIR. Diffuse reflectance FTIR spectra of outlet gases were measured by using a Perkin–Elmer Spectrum One FTIR spectrometer. The recorded IR spectra were operating in the spectral range 4000–700 cm^{-1} at a resolution of 4 cm^{-1} with the use of Time Base 2.0 software. The desulfurization capacity of Fe_2O_3/SiO_2 sorbents was calculated by the equation of sorbent utilization (SU):

$$\mathrm{SU}(\%) = \frac{\int_0^t (C_{\mathrm{in}} - C_{\mathrm{out}})\mathrm{d}t}{C_{\mathrm{in}} \times t^*} \times 100\% \tag{1}$$

where C_{in} and C_{out} are the inlet and outlet concentrations of H_2S (ppm), respectively; t is the experimental breakthrough time (min), and t^* is the theoretical breakthrough time (min) of the process. The experimental breakthrough time was defined as the time from the beginning of the experiment to the point when the outlet H_2S concentration reached 100 ppm, which is 1% of the inlet H_2S concentration.

The theoretical breakthrough time (min) was calculated by the equation:

$$t^* = \frac{\left(\frac{WX}{M}\right)A}{F} \tag{2}$$

where W is the weight of the sorbent placed in the reactor (g), X is the actual weight loading of iron oxide supported on SiO_2 (g g^{-1}), M is the molecular weight of the iron oxide (g mol^{-1}), A is the moles of H_2S that can be absorbed by one mole of iron oxide (mol mol^{-1}), and F is the molar flow rate of the inlet H_2S (mol min^{-1}).

3. Results and discussion

3.1. Temperature-programmed reduction

The TG/DTA curves as a function of temperature for the 10 wt.% Fe_2O_3/SiO_2 sorbent with 15% H_2 in N_2 are displayed in Fig. 1. In the TG curve, the sorbent can be assigned into three stages. First, a small weight loss (0.5%) of the sorbent accompanies an exothermic process at about 323–473 K, which is attributed to the evaporation of adsorbed water (Tan et al., 2012). The weight loss (0.4%) in the second stage can be attained at 693–773 K that is due to the reduction of hematite to magnetite (Pineau et al., 2006).

$$3Fe_2O_{3(s)} + H_{2(g)} \leftrightarrow 2Fe_3O_{4(s)} + H_2O_{(g)} \tag{3}$$

As the calcination temperature increases, the third weight loss about 0.6% occurs in the temperature range of 773–953 K, which is caused by the formation of iron oxide from magnetite (Munteanu et al., 1997).

$$Fe_3O_{4(s)} + H_{2(g)} \leftrightarrow 3FeO_{(s)} + H_2O_{(g)} \tag{4}$$