Regeneration behavior of tin oxide sorbent for warm syngas desulfurization

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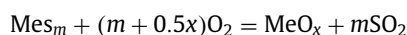
A B S T R A C T

The steam regeneration and SO_2 regeneration of tin oxide for warm syngas desulfurization is studied in the temperature range of 400–600 °C. In the steam regeneration, reversible removal of H_2S achieved. Regenerated H_2S concentration increased with the increasing regeneration temperature. SnO_2 sorbent can achieve a complete regeneration by steam at 500 and 600 °C. In the SO_2 regeneration, elemental sulfur was produced by the reaction of SnS and SO_2. Raising the regeneration temperature (500–600 °C) or SO_2 concentration (1.5–10 vol%) improved the regeneration rate. Under SO_2 regeneration at 500 °C, SnS_2 formed in the sorbent due to the interconversion of tin sulfides. Under steam regeneration or SO_2 regeneration, the cyclic breakthrough sulfur capacity of SnO_2 sorbent decreased because of the sintering caused by low melting component SnS. A two-stage regeneration process was applied to recover the elemental sulfur which achieved a complete regeneration.

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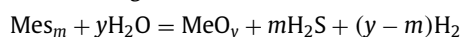
1. Introduction

Hydrogen production from coal syngas based on H_2/CO_2 separation after the water gas shift reaction is a promising technology for advanced coal utilization due to its advantages of high efficiency and low emissions. However, coal syngas usually contains 0.2%–1.0% H_2S and other sulfur compounds [1]. Desulfurization is a crucial process because H_2S is not only harmful to human health but also causes catalyst poisoning and equipment corrosion. Hot syngas desulfurization uses metal oxides or mixed metal oxides as sorbent and the process consists of sulfidation and regeneration. The regeneration process is critical for the sorbent selection. There are three ways to regenerate the sulfided sorbents with different sulfur products.
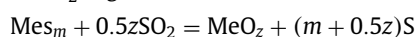
Oxygen regeneration:

$$Mes_m + (m + 0.5x)O_2 = MeO_x + mSO_2$$

Steam regeneration:

$$Mes_m + yH_2O = MeO_y + mH_2S + (y - m)H_2$$

SO_2 regeneration:

$$Mes_m + 0.5zSO_2 = MeO_z + (m + 0.5z)S$$

Oxygen is the most common way for the regeneration. ZnO [3], CuO [4] and MnO [5] can be regenerated under O_2 atmosphere. However, the reaction is very exothermic. In order to control the regeneration temperature, a diluted oxygen or air must be used which results in the diluted SO_2 [2]. SO_2 is another pollutant and requires a further treatment. The formation of sulfate is also unfriendly to oxygen regeneration. H_2S is the product in the steam regeneration. Wakker et al. chose Mn/γ-Al_2O_3 and Fe/γ-Al_2O_3 as candidates for steam regeneration [6]. For Mn/γ-Al_2O_3, $MnAl_2O_4$ formed during the preparation. Compared with MnO, $MnAl_2O_4$ absorbed H_2S more weakly which could be regenerated with H_2O. However, the sensitivity of H_2O in the sulfidation and large amounts of steam consumption in the regeneration are two major drawbacks. The direct production of elemental sulfur is possible in the SO_2 regeneration. Bakker et al. tested Mn-based sorbent regeneration by SO_2 to recover elemental sulfur, but the regeneration was not complete [7]. An excess diluted O_2 regeneration was needed to regenerate the strong sites. The research of Zeng et al. pointed out that reduced CeO_2 was efficient for hot syngas desulfurization [8,9]. The sulfided product, Ce_2O_2S reacted with SO_2 to produce element sulfur directly over the range of 500–700 °C. Compared with Mn-based sorbents, SO_2 regeneration of Ce-based sorbent was rapid and complete. Fe_2O_3 has a poorer desulfurization performance than ZnO, but it is superior in the regeneration process. All the mentioned regeneration methods could be applied to regenerate the sulfided Fe-based sorbents [10–12].

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Nomenclature

q	amount of sulfur absorbed by the sorbent (mg/g)
$Q_{\text{sulfidation}}$	total feed gas flowrate in the sulfidation (mL/min)
$Q_{\text{regeneration}}$	total feed gas flowrate in the regeneration (mL/min)
M_{sorbent}	weight of sorbent (g)
m_s	weight of elemental sulfur collected (g)
x_{in}	inlet sulfurous gas volume fraction (%)
x_{out}	outlet sulfurous gas volume fraction (%)
$x_{\text{re,dry}}$	outlet H_2S volume fraction in the regeneration (%, dry base)
t	breakthrough time (min)
t_1	sulfidation time (min)
t_2	regeneration time (min)
R_{H_2S}	H_2S recovery (%)
R_S	elemental sulfur recovery (%)

In the steam regeneration, the main product was Fe_3O_4 and H_2S, while in the SO_2 regeneration, elemental sulfur was obtained and Fe_3O_4 was slowly oxidized to Fe_2O_3. The direct elemental sulfur production by SO_2 regeneration is more attractive which avoids the further treatment of sulfur product.

In the previous studies, SnO_2 is not within the scope of research because SnO_2 is reduced to a low-melting tin in a high reducing atmosphere at the high temperature [13]. Droog et al. suggested that desulfurization operated at moderate temperatures of 343–538 °C could be better because the capital and operation cost was lower and the overall IGCC process efficiency improved only a little [14]. At moderate temperatures, the reduction of SnO_2 will not be a big problem. SnO_2 has a favorable regeneration characteristic that both steam regeneration and SO_2 regeneration are possible for SnO_2 sorbent [15,16]. Haldor Topsøe (Denmark) used a high pressure steam to regenerate SnS at 500 °C and received a 2%–3% H_2S in the outlet. They did not focus on the detailed study of steam regeneration characteristics. TDA (USA) took a SO_2 containing gas from the regeneration of ZnS by diluted O_2 to the SnS bed and elemental sulfur was obtained at 700 °C. However, SnO_2 occupied the lower part of the sorbent bed in their study, so the concentration of regeneration gas for SnO_2 contained excess O_2 and SO_2 was uncertain.

The objective of this work was to study the regeneration performance of SnO_2 sorbent and present the characteristics of steam regeneration and SO_2 regeneration. The influence of regeneration operation factors (i.e. temperature) and the physical and chemical properties of SnO_2 sorbent after regeneration were investigated. The cyclic desulfurization performance of SnO_2 sorbent and the improvement of the regeneration method were also discussed.

2. Experimental

2.1. Preparation of sorbents

SnO_2 sorbent used in the experiments was an analytical reagent from Sinopharm Chemical Reagent. Before sulfidation tests, SnO_2 sorbent was pressed and sieved through 97–150 μm. The commercial SnO_2 was treated in a 100 mL/min 50 vol% H_2, and balanced N_2 flow at 400–500 °C for 3 h. The treated sorbent was analyzed by X-ray photoelectron spectroscopy (XPS).

Table 1. Regeneration conditions used in regeneration tests.

	Steam regeneration	SO_2 regeneration
Temperature (°C)	400, 500, 600	500, 550, 600
Pressure (MPa)	0.1	0.1
Flowrate (mL/min)	60	60
Gas composition	H_2O: 50 vol%; N_2: balance	SO_2: 1.5 vol%, 5 vol%, 10 vol%; N_2: balance

2.2. Characterization of sorbents

The XPS analyses were performed using an ESCALAB 250Xi spectrometer manufactured by Thermo Fisher. A non-monochromatic Al $K\alpha$ X-ray source was used, and samples were analyzed as pellets. The phase composition analysis of the sorbents using X-ray diffraction (XRD) was determined on a Rigaku D-max 2500 X-ray diffractometer with Cu $K\alpha$ radiation. The experimental data was digitally collected by a "step by step" scanning method in a 2θ angle interval of 10°–70°. The textural properties of the sorbents using Brunauer–Emmett–Teller (BET) theory and Barret–Joyner–Halenda (BJH) model were performed on an ASAP 2020 (Micromeritics, USA) by determining the nitrogen adsorption-desorption isotherms at –196 °C. The sorbent surface morphology was determined by a scanning electron microscopy (ZEISS MERLIN VP compact, Germany).

2.3. Sulfidation and regeneration tests of SnO_2

The sulfidation and regeneration tests of SnO_2 were evaluated in a fixed-bed reactor with an inside diameter of 10 mm. 1.0 g of SnO_2 was charged into the reactor and heated to 400 °C in a N_2 atmosphere. Before the sulfidation, SnO_2 was reduced by a 50 vol% H_2 and balanced N_2 for 1 h. Then, a feed gas containing 0.5 vol% H_2S, 50 vol% H_2 and balanced N_2 was introduced from the top of the reactor with a flowrate of 60 mL/min. The concentrations of H_2S in the inlet and outlet were analyzed by a gas chromatograph (GC-9A, Shimadzu) equipped with a flame photometry detector (FPD). Since GC-9A was applied for low concentration analysis, an inert N_2 was used to dilute the gas concentration to 1/10 of the original gas concentration. The breakthrough point (BT point) was defined as the time when the outlet H_2S concentration reached 50 ppmv, which is 1% of the inlet H_2S concentration in the feed gas. The amount of sulfur absorbed by the sorbent was calculated by the following equation:

$$q = \frac{32}{22.4} \times \frac{Q_{\text{sulfidation}}}{M_{\text{sorbent}}} \times \int_0^{t_1} (x_{\text{in}} - x_{\text{out}}) \mathrm{d}t_1$$

After sulfidation, the sulfided sorbent was regenerated at 400–600 °C. The regeneration conditions are presented in Table 1. In the steam regeneration, the steam was produced by heating the water and the flowrate of water was controlled by a pump (LabAlliance). The outlet gas flew through the screwed quartz tube in the ice water to remove steam and analyzed by GC-9A. The H_2S recovery R_{H_2S} was obtained by the following equation:

$$R_{H_2S} = \frac{\frac{32}{22.4} \times 50\% \times Q_{\text{regeneration}} \times \int_0^{t_2} x_{\text{re,dry}} \mathrm{d}t_2}{M_{\text{sorbent}} \times q} \times 100\%$$

$$= \frac{50\% \times Q_{\text{regeneration}} \times \int_0^{t_2} x_{\text{re,dry}} \mathrm{d}t_2}{Q_{\text{sulfidation}} \times \int_0^{t_1} (x_{\text{in}} - x_{\text{out}} \mathrm{d}t_1)} \times 100\%$$

In SO_2 regeneration, the outlet gas flew through the U-tube with quartz wool in the ice water to condense the elemental sulfur and analyzed by GC-9A. The condensed sulfur in the U-tube