



Steam regenerative removal of hydrogen sulfide from hot syngas by a novel tin oxide and yttrium oxide sorbent



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ABSTRACT

A novel H_2S sorbent based on SnO_2 and Y_2O_3 is developed by a co-precipitation method for steam regenerative removal of H_2S from hot syngas at moderate temperatures (400–500 °C). SnO_2 - Y_2O_3 sorbent is stable in a reducing atmosphere (i.e. 500 °C, 50% H_2) and achieves a 99.9% H_2S removal during successive desulfurization and regeneration cycles. The addition of yttrium to SnO_2 decreases the reduction property of SnO_2 and no metallic Sn exists in the reducing atmosphere due to the formation of a pyrochlore-type compound, $Y_2Sn_2O_7$. The SnO_2 - Y_2O_3 sorbent has a desulfurization performance deterioration with the increasing calcination temperature. The newly developed SnO_2 - Y_2O_3 sorbent can be regenerated by steam at 500 °C. In the eight successive desulfurization and regeneration cycles, SnO_2 - Y_2O_3 sorbent has a cyclic breakthrough sulfur capacity of 9 mg/g without significant sulfur capacity loss.

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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]. H_2S is a hazardous gas that is not only harmful to human health but also causes catalyst poisoning and equipment corrosion. Hence, H_2S removal from syngas is one of the key processes in a hydrogen production system. To avoid an energy penalty in the process of cooling the syngas to ambient temperature for solvent absorption and reheating the cleaned syngas for gas turbine combustion, high-temperature desulfurization by pure or mixed metal oxides, such as ZnO [2,3], Fe_2O_3 [4,5], MnO [6,7], ZnO - TiO_2 [8–11], ZnO - Fe_2O_3 [12,13], and CuO - Cr_2O_3 [14,15], has been intensively studied.

Droog et al. [16] suggested that desulfurization operated at moderate temperatures of 343–538 °C could be better because the capital and operation cost is lower and the overall IGCC process efficiency improves only a little. The sorbent regeneration characteristics are vital to the hot syngas desulfurization using metal

oxides. Oxygen regeneration is widely applied for most metal sulfides in the literature, but only some can be regenerated by steam. The oxygen regeneration 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 . The advantages of steam regeneration include: 1) an endothermic effect that protects the sorbent from sintering, 2) depression of sulfate formation, and 3) a high concentration of H_2S as the product. Tamhankar et al. [17] studied the steam regeneration of $FeS_{1.1}$ and confirmed the formation of Fe_3O_4 and H_2S as products. Wakker et al. [18] prepared MnO/γ - Al_2O_3 and FeO/γ - Al_2O_3 by impregnation and proved that the active compounds $MnAl_2O_4$ and $FeAl_2O_4$ made steam regeneration possible at 600 °C. SnO_2 is another steam regenerative H_2S sorbent at moderate temperatures developed by Haldor Topsøe (Denmark) [19]. The oxidation of SnS back to SnO_2 by steam is typically done at 450–500 °C, which makes SnO_2 attractive for steam regenerative desulfurization research at moderate temperatures. TDA Research [20] proposed using SnO_2 as the first sorbent and ZnO -based sorbent as the second sorbent to convert H_2S into elemental sulfur. In the regeneration, steam and SO_2 from ZnS regeneration were used to regenerate SnS .

However, SnO_2 is easily reduced to metallic Sn in a reducing atmosphere [21]. Metallic Sn is in the liquid state when the temperature is above 231.9 °C, which is unfavorable for desulfurization due to active compound loss and structure damage to the SnO_2

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sorbent. Steam in the feed syngas is helpful to avoid the reduction of SnO₂, which was found by Haldor Topsøe [19]. However, a high steam content in the syngas restricts the desulfurization efficiency [22]. The stabilization of metal oxides against complete reduction by introducing other metals has been investigated extensively in other metal oxide sorbents. The addition of TiO₂ to ZnO can reduce the tendency for ZnO reduction and the subsequent volatilization of metallic Zn, thereby increasing the maximum sorbent operation temperature [8–11]. The formation of CuCr₂O₄ in the CuO–Cr₂O₃ sorbent is responsible for preserving some copper in the Cu²⁺ or Cu⁺ oxidation state, which accounts for the high H₂S removal efficiency [14,15]. For SnO₂, a study of CO and CH₄ oxidation showed that the introduction of yttrium into SnO₂ could decrease the H₂ reduction performance of SnO₂ by the formation of a pyrochlore compound, Y₂Sn₂O₇ [23]. However, the prevention of metallic Sn formation of this material was unknown.

In this study, a novel Sn–Y sorbent was synthesized for steam regenerative H₂S removal in a reducing atmosphere. The structural features of the Sn–Y sorbent were characterized by X-ray diffraction (XRD). The reduction performance of the Sn–Y sorbent was analyzed by H₂-temperature programmed reduction (TPR) and X-ray photoelectron spectroscopy (XPS). The desulfurization and regeneration performance of the Sn–Y sorbent were investigated in a fixed-bed reactor.

2. Experimental

2.1. Preparation of sorbents

The SnO₂–Y₂O₃ sorbents were prepared by a co-precipitation method at room temperature. 0.06 mol of SnCl₄·5H₂O and Y(NO₃)₃·6H₂O with a Sn/Y atomic ratio of 1:2 were dissolved in 50 mL of deionized water. Then, a 5 mol L⁻¹ ammonia solution was added to the solution with vigorous stirring to adjust the pH to 9. The resultant slurry was maintained for 3 h before the mixture was filtered by vacuum filtration and washed with deionized water until the pH was 7. Finally, the precipitate was dried in air at 105 °C overnight and was calcined at 500, 600, 700, and 800 °C for 6 h. All of the prepared sorbents were crushed and sieved through 97–150 μm. The resultant SnO₂–Y₂O₃ sorbents were assigned as Sn2Y–x (x = calcination temperature). The SnO₂ used in the experiment was an analytical reagent from Sinopharm Chemical Reagent.

2.2. Characterization of sorbents

The phase composition analysis of the sorbents by XRD was conducted on a Rigaku D-max 2500 X-ray diffractometer using Cu Kα radiation. The experimental data were digitally collected by a “step-by-step” scanning method in the 2θ angle interval of 10–90°.

The textural properties for sorbents were determined on an ASAP 2020 (Micromeritics, USA) by determining the nitrogen adsorption–desorption isotherms at –196 °C. Prior to the analysis, the samples were heated to 250 °C under vacuum and held for 180 min. The BET specific surface area and pore volume were assessed from the adsorption data. The mean pore diameter was determined by applying the Barret–Joyner–Halenda (BJH) model to the isotherm desorption branch.

XPS analyses were performed using an ESCALAB 250Xi spectrometer manufactured by Thermo Fisher. A non-monochromatic Al Kα X-ray source was used, and samples were analyzed as pellets. Before the XPS analyses, 3.0 g sample was treated in a 100 mL min⁻¹ 50% H₂/50% N₂ flow at 400 or 500 °C for 3 h.

The H₂-TPR experiment was analyzed by an AutoChem II 2920 (Micromeritics, USA). In the H₂-TPR experiments, a 25 mg sample

was first treated in pure Ar from room temperature to 250 °C and held for 3 h at 250 °C to remove moisture and physisorbed gases, and then cooled to room temperature. A 20 mL min⁻¹ mixture containing 10% H₂ and Ar was introduced through the sample until the outlet gas composition reached that of the inlet gas. Then, the temperature was increased from room temperature to 1050 °C at a rate of 10 °C min⁻¹. The change of the H₂ content in the outlet gas was detected by gas chromatograph (GC) with a thermal conductivity detector (TCD).

2.3. Desulfurization and regeneration tests of sorbents

The desulfurization and regeneration tests of the sorbents were evaluated in a fixed-bed reactor with an inside diameter of 10 mm. Approximately 2.7 g of the sorbent was charged into the reactor and heated to 400 °C in a N₂ atmosphere. Then, feed gas containing 0.5% H₂S, 50% H₂ and balanced N₂ was controlled by mass flowmeters (D07-11C Beijing Sevenstar Electronics) and introduced from the top of the reactor with a gas hourly space velocity (GHSV) of 2000 h⁻¹. The concentration of H₂S in the outlet was analyzed by a gas chromatograph (GC-9A, Shimadzu) equipped with a flame photometry detector (FPD). The breakthrough time is defined as the time when the outlet H₂S concentration reaches 50 ppmv. The breakthrough sulfur capacity *q* of the sorbents was calculated by the following equation:

$$q \left(\frac{\text{mg sulfur}}{\text{g sorbent}} \right) = \frac{Q_{\text{feed gas}} M_{\text{sulfur}}}{m_{\text{sorbent}} V_{\text{mol}}} \times \left[\int_0^t (C_{\text{in}} - C_{\text{out}}) dt \right]$$

where $Q_{\text{feed gas}}$ is the total feed gas flowrate in mL min⁻¹, M_{sulfur} is the atomic weight of sulfur (32 g mol⁻¹), m_{sorbent} is the weight of sorbent, V_{mol} is the molar volume in L mol⁻¹ under standard conditions of 273.15 K and 1 atm (22.4 L mol⁻¹), C_{in} and C_{out} are the inlet and outlet H₂S concentration (%), respectively, and t is the breakthrough time in minutes.

The desulfurization and regeneration test was conducted on the Sn2Y-700 sorbent. The sulfided sorbent was regenerated at 500 °C by a steam regeneration method. Regeneration gas containing 50% H₂O/50% N₂ with a GHSV of 4000 h⁻¹ was introduced to the sulfided sorbents until less than 10 ppmv H₂S in the regeneration gas was detected by GC. Then, the reactor was purged with N₂ for the next desulfurization.

3. Results and discussion

3.1. Characterization of the prepared sorbents

The phase composition of pure SnO₂ and Sn2Y sorbents was analyzed by XRD and the results are shown in Fig. 1. Commercial SnO₂ has typical diffraction peaks (PDF: 41–1445), shown in Fig. 1(a). For Sn2Y sorbents in Fig. 1(b), when the calcination temperature is 500 or 600 °C, the sorbents are mainly amorphous. If the calcination temperature increases to 700 or 800 °C, there are sharp and strong peaks in their XRD patterns, which are assigned to the Y₂Sn₂O₇ (PDF: 88–0445). However, a left shift of all the characteristic peaks of Y₂Sn₂O₇ is observed in both Sn2Y-700 and Sn2Y-800 sorbents. Since the Sn/Y atomic ratio is 1:2, there is excess Y₂O₃ formed in the sorbents. In the sample of Sn2Y-800, the peaks of Y₂O₃ (PDF: 41–1105) is also observed. Since the peaks of Y₂O₃ and Y₂Sn₂O₇ are very close, the excess Y₂O₃ causes the peak shift of Y₂Sn₂O₇. In the Sn2Y sorbents, Y₂O₃ reacts with SnO₂ to form a new species which has the pyrochlore-type structure A₂B₂O₇ [24]. According to the XRD results, 700 °C is the proper calcination temperature for the formation of Y₂Sn₂O₇ in this sorbent preparation

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