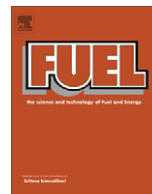




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## Simultaneous removal of hydrogen sulfide and mercury from simulated syngas by iron-based sorbents

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### ABSTRACT

Two iron oxide based sorbents, TG-1 and TG-F, with high desulfurization efficiency, were selected for simultaneous removal of H<sub>2</sub>S and Hg from simulated syngas. Our evaluation tests were carried out using a fixed bed reactor at different temperatures and in ambient atmosphere. The different activities for the simultaneous removal of H<sub>2</sub>S and Hg between TG-1 and TG-F or TG-1-S (denoted as such after uptake of H<sub>2</sub>S) were compared. The results show that the two iron oxide based sorbents can capture Hg effectively from simulated syngas. The preferred temperature for Hg removal using the TG-F and TG-1 sorbents are 60–120 °C and 100–140 °C, respectively. The Hg absorption capacity of TG-1 is higher than that of TG-F under the same conditions. CO and H<sub>2</sub> in the feed gas have negligible effect on the efficiency of Hg removal. H<sub>2</sub>S is favoured for the removal of Hg over iron-based sorbents and it was found that the influence of H<sub>2</sub>S concentration on the Hg capacity of the TG-1 and TG-F sorbents are different. It is found that the main active components of the two sorbents during the reaction are different. After several desulfurization cycles, the TG-1-S sorbent has a high efficiency for Hg removal from the simulated syngas.

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### 1. Introduction

Due to the great harm it does to the environment and human health, mercury pollution is considered as the top of the list of environmental pollutants by the World Health Organization [1,2]. There are three forms of mercury in gas, elemental mercury (Hg<sup>0</sup>), gaseous oxidized mercury (Hg<sup>+</sup> and Hg<sup>2+</sup>) and particulate-bound mercury (Hg<sup>p</sup>) [3]. Gaseous oxidized mercury and particulate-bound mercury can be efficiently removed by wet desulfurization and dust removal devices [4]. Due to its extreme insolubility in water, high vapor pressure, and semi-noble metal properties, elemental mercury vapor is difficult to capture [5].

One of the major sources of anthropogenic mercury emissions are coal conversion processes [6] such as combustion, gasification, liquefaction and coking. Nowadays, almost all mercury control technologies, both practical and fundamental, focus on the removal of Hg from flue gas. As one of the most efficient coal cleaning technologies, coal gasification will be widely used in the future. It has been reported that more elemental Hg and higher concentrations of Hg are emitted from coal gasification processes than from coal combustion [7]. In addition, a reducing environment is not

favorable for Hg oxidation via gas-phase reactions [8]. Therefore, mercury control technology for coal gasification is very important.

Another environmental pollutant in coal-based gas is H<sub>2</sub>S, which has received more attention than any other. It is the main precursor to acid rain and causes severe corrosion to most systems involved with coal gasification, such as power plants and synthetic gas conversion plants [9–12]. More research has been carried out on the removal of H<sub>2</sub>S from coal-based gas than the removal of Hg. Currently, this research is mainly focused on the reactions of H<sub>2</sub>S with metal oxides such as iron, calcium, copper, zinc and manganese to produce the corresponding metal sulfide [13–15].

A study of Hg<sup>0</sup> removal from coal-derived fuel gas at elevated temperature (204–315 °C), using candidate sorbents, has been carried out; however, the exact compositions of the sorbents were not given [16]. Some previous work has reported that supported noble metals, such as palladium, can be used for capturing mercury, arsenic, selenium and phosphorus from simulated fuel gases at elevated temperatures [1,17–21]. Fuel gas constituents, such as moisture and hydrogen sulfide, can have either promotional or poisoning effects on the capture of mercury, arsenic, selenium and phosphorus [18,22,23]. Recent tests at a pilot gasifier showed that a palladium sorbent removed nearly 100% of the mercury, arsenic and phosphorus from dirty streams of fuel gas over several weeks [17–19].

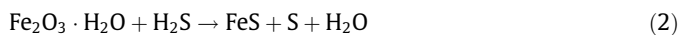
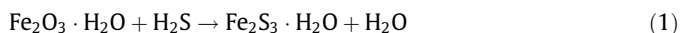
Recently, iron-based sorbents such as iron oxide (Fe<sub>2</sub>O<sub>3</sub>), supported iron oxides on TiO<sub>2</sub>, and iron sulfides have been

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proposed as active mercury sorbents.  $\text{Hg}^0$  reacts with  $\text{H}_2\text{S}$  to form  $\text{HgS}$  during the removal of elemental mercury from simulated coal-derived gases [24–26]. The iron-based sorbents have the advantage of being significantly cheaper than noble metal sorbents.

The removal of  $\text{H}_2\text{S}$  from simulated syngas with iron oxide sorbents is a classic and effective desulfurization method and is widely used due to its advantages of high sulfur capacity, low cost, simple and easy operation [27,28]. At room temperature, the desulfurization reactions of iron oxide sorbents are shown to be as follows [28]:



For room temperature desulfurization, iron oxide sorbents are usually discarded after reaching their desulfurization capacity. It may be of considerable additional value if these used iron oxide sorbents, with plenty of elemental sulphur and  $\text{FeS}_x$ , could be used for the capturing of elemental mercury in coal-based gas. Most sorbents can only remove one kind of pollutant, such as  $\text{H}_2\text{S}$  or  $\text{Hg}$ .

On the basis of the above analysis, iron oxide sorbents may be a candidate for simultaneous capture of  $\text{H}_2\text{S}$  and  $\text{Hg}$ . In this paper, two kinds of commercial iron oxide desulfurizer (TG-F and TG-1) have been used as sorbents for the simultaneous removal of  $\text{Hg}$  and  $\text{H}_2\text{S}$ . Evaluation tests were carried out using a fixed bed reactor. The effect of temperature and ambient atmosphere on the simultaneous removal of  $\text{Hg}$  and  $\text{H}_2\text{S}$  has been investigated. In addition, the TG-1 sorbent after uptake of  $\text{H}_2\text{S}$  (denoted as TG-1-S) is also used as an adsorbent for the simultaneous removal of  $\text{Hg}$ . The differences between TG-1-S and TG-1 are discussed.

## 2. Experimental

### 2.1. Sorbent samples

Two commercial iron oxide desulfurizers, known as TG-1 and TG-F, were supplied by Shanxi Clean Catalyst & Purification Technology Development Company. Both have high efficiency for the removal of  $\text{H}_2\text{S}$  from simulated syngas at ambient temperature. They were selected and used as the experimental samples for evaluating their capacity for the removal of  $\text{Hg}$  and  $\text{H}_2\text{S}$ . Physical parameters and ash analyses of the two sorbents are shown in Tables 1 and 2. The tables show that both TG-1 and TG-F contain iron oxide as the main active ingredient together with other, different components. The TG-1 sorbent after uptake of  $\text{H}_2\text{S}$  is denoted as TG-1-S. The S content of TG-1-S and TG-1 are 22.82 wt% and 9.89 wt%, respectively.

### 2.2. Apparatus and procedure

A schematic diagram of the experimental apparatus is shown in Fig. 1. It consists of the devices for  $\text{Hg}$  generation, evaluation of  $\text{Hg}$  and  $\text{H}_2\text{S}$  removal and the detection system. The  $\text{Hg}$  generating device includes a  $\text{Hg}$  permeation tube (US VICI Company), glass beads, U-tube and super constant temperature water bath. The permeation tube was loaded at the right hand side of the U-tube, which was maintained at  $25 \pm 0.5^\circ\text{C}$  in the water bath. The  $\text{Hg}$  per-

meation tube is a source of  $\text{Hg}$  vapor, and glass beads in the U-tube are used for heating the carrier gas.  $\text{Hg}$  vapor was brought into the  $\text{Hg}$  and  $\text{H}_2\text{S}$  removal evaluation device using a carrier of ultrahigh-purity  $\text{N}_2$ . The flow rate through the U-tube was controlled by a mass-flow controller.

The evaluation of  $\text{Hg}$  and  $\text{H}_2\text{S}$  removal was carried out in a fixed bed adsorption device, with PID controller, used to maintain the bed at a fixed temperature with  $0.5^\circ\text{C}$  precision.  $200 \pm 5$  mg sorbents, with a particle size of 40–60 mesh, were placed in the level quartz tube reactor (5 mm internal diameter) for each experiment. All pipelines were maintained at a fixed temperature using heating tape. The gas flow rate was controlled by a mass flow controller at 400 ml/min. The initial concentration of mercury was  $60 \pm 3 \mu\text{g}/\text{m}^3$ .  $\text{Hg}$  in the exhaust gas was directed to an activated carbon trap before being expelled into the air. A gas chromatograph equipped with a flame photometry detector (FPD) was used as the  $\text{H}_2\text{S}$  detector. The elemental  $\text{Hg}$  detector was a QM201-H mercury analyzer, made by Suzhou Greencalm Instruments Limited. It can continuously monitor elemental  $\text{Hg}$  with a minimum detection limit of less than  $1 \mu\text{g}/\text{m}^3$ .

Mercury removal efficiency ( $\eta$ ) were defined for the evaluation of mercury removal by the sorbents as:

$$\eta = (n_0 - n_1)/n_0 \times 100\%$$

where  $n_0$  and  $n_1$ , in  $\mu\text{g}/\text{m}^3$ , are the  $\text{Hg}$  concentrations in the feed and effluent gases, respectively.

The surface area was determined via nitrogen adsorption at 77 K using a Micromeritics ASAP2000 analyzer. XPS analysis was conducted for determination of the surface elemental concentration of samples with an ESCALAB 250 spectrometer (VG Scientific Ltd., UK) equipped with an Al K $\alpha$  source ( $h\nu = 1486.6$  eV).

## 3. Results and discussion

### 3.1. Effect of temperature on the simultaneous removal of $\text{H}_2\text{S}$ and $\text{Hg}$

The results of the  $\text{Hg}$  adsorption by TG-F and TG-1 in a  $\text{N}_2$  atmosphere with 300 ppm  $\text{H}_2\text{S}$  at different temperatures are shown in Fig. 2. This shows that the efficiency of  $\text{Hg}$  removal by TG-F varies as the temperature changes. The efficiency of  $\text{Hg}$  removal is 55% and 60% for more than 8 h at 60 and  $80^\circ\text{C}$ , respectively. At  $120^\circ\text{C}$  and  $140^\circ\text{C}$ , the  $\text{Hg}$  removal efficiency decreases from 80% to 40%, and 80% to 10% after 8 h, respectively. At  $160^\circ\text{C}$ , the sorbent was totally deactivated in 3 h. This indicates that the TG-F sorbent is good for  $\text{Hg}$  removal when the reaction temperature is in the range  $80$ – $120^\circ\text{C}$ .

The  $\text{Hg}$  removal efficiency of TG-1 is 65% at  $80^\circ\text{C}$ , and this could be maintained for more than 10 h. At  $100$ – $120^\circ\text{C}$ , the  $\text{Hg}$  removal efficiency of TG-1 is above 80% over 10 h. In contrast, at  $140^\circ\text{C}$ , the  $\text{Hg}$  removal efficiency can only be maintained for 5 h above 80%, after which it decreases to 65%. At  $160^\circ\text{C}$ , the sorbent was totally deactivated in 5 h.

The  $\text{Hg}$  capacities of TG-1 and TG-F sorbents at different temperatures are presented in Table 3. This shows that the  $\text{Hg}$  capacity decreases as the temperature rises. In addition, the  $\text{Hg}$  capacities of TG-1 are twice as large as those of TG-F.

The  $\text{H}_2\text{S}$  adsorption curves of the TG-F sorbent at different temperatures are presented in Fig. 3. This shows that the efficiency of  $\text{H}_2\text{S}$  removal increases as the temperature rises. The TG-F sorbent is deactivated for the  $\text{H}_2\text{S}$  removal reaction in 6.5 h at  $120^\circ\text{C}$  and  $140^\circ\text{C}$ . At  $160^\circ\text{C}$ , the TG-F sorbent works for 6.5 h with a  $\text{H}_2\text{S}$  removal efficiency of 70%.  $\text{H}_2\text{S}$  adsorption curves of the TG-1 sorbent at different temperatures are also presented in Fig. 3. At  $120^\circ\text{C}$ , the  $\text{H}_2\text{S}$  removal efficiency decreases dramatically and shows only tiny reductions at  $140^\circ\text{C}$  in 10 h. At  $160^\circ\text{C}$ , the  $\text{H}_2\text{S}$  removal efficiency

**Table 1**  
Physical parameters of TG-1 and TG-F sorbents.

Sorbents	Physical parameters		
	BET surface area ( $\text{m}^2/\text{g}$ )	Bulk density ( $\text{g}/\text{mL}$ )	Porosity (%)
TG-1	60	0.7–0.8	40–50
TG-F	57	0.5–0.6	50–60

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