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# High performance of Fe nanoparticles/carbon aerogel sorbents for $H_2S$ Removal

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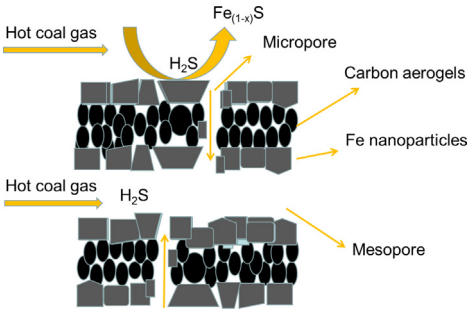
## HIGHLIGHTS

- As-prepared Fe nanoparticles (NPs) sorbent were not significantly affected by the CO and $H_2$.
- The activities of the as-prepared sorbent with different carbon aerogel were tested.
- 50%Fe/C700 sorbent had the highest sulfur capacity of 12.54 g S/100 g sorbent.

## GRAPHICAL ABSTRACT

Fe Nanoparticles inlaid carbon aerogel and the process diagram of high temperature desulfurization.

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## ABSTRACT

To solve the effect of the strong reduction gas, sintering problem and improve the desulfurization activity. Fe nanoparticles (NPs) into carbon aerogel desulfurizers were fabricated with by 50%Fe/C700 precursor and their performance for $H_2S$ removal in hot coal gas was studied. The Fe nanoparticles loading in mesoporous carbon aerogels with larger specific surface area and pore volume sorbent were designed and firstly applied to remove $H_2S$ with high efficiency in hot coal gas. The $H_2S$ removal experiments were conducted in the temperature range of 500–650 °C using hot coal gas containing 0.2 vol% $H_2S$. We explored the optimum temperature conditions and the influence of textural parameters of carbon aerogels and tested the Fe nanoparticles desulfurizers with 10–20% $H_2$ and 10–20% CO. The fresh, used, regenerated samples were characterized by $N_2$ adsorption, X-ray diffraction, high-resolution scanning electron microscope techniques (HRSEM) and high resolution transmission electron microscopy (HRTEM). The results confirmed that Fe nanoparticle sorbent had high desulfurization performance. This work could provide a new direction and new field in hot coal gas desulfurization and would be important to research on the development sector of the coal industry.



## 1. Introduction

From a global perspective, coal will still be the major fuel of electric power plants because of its sufficient resource [1].

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However, the conventional coal-fired systems can produce atmospheric pollutants such as dust, sulfur compounds and so on. In consideration of environment protection and thermal efficiency, integrated gasification combined cycle (IGCC) is considered to be the most promising and environmental friendly technological methods for the generation of power from coal [2]. In coal gasification process, sulfur is converted to hydrogen sulfide, which would cause severe corrosion of downstream equipment, the sulfur compounds have to be removed prior to utilization. In the conventional methods for $H_2S$ removal, wet absorption or zinc oxide sorption, the disadvantage is that the hot coal gas has to be cooled down to ambient temperature for sulfur removal and then heated up to a required temperature for burning in gas turbine [3]. For better thermal efficiency and lower the capital costs of IGCC system, the hot coal gas desulfurization (HGD) technique has obtained increasing attention [4].

High temperature coal gas cleaning has been researched in recent years by using various metal-based sorbents such as oxides of Mn, Zn, Cu, Ca, Co and Ce, studying as desulfurizers for the direct removal of $H_2S$ [5–11]. However, the utilization of the metal oxides is limited because of the low specific surface area and pore volume, and the sulfide formed during adsorption processes would lead to the blocking of pores, resulting in the decline in $H_2S$ removal. To solve these problems, natural zeolites and rare-earth oxides $SiO_2$ were added to metal oxides or their mixtures as structure stabilizer [12]. However, when $SiO_2$ was used as support, the desulfurization performance declined due to chemical interaction between support and active component, and the strong interaction also led to difficulty in the regeneration of active species [10]. With regard to using some microporous zeolites as support, there is severe limitation in mass transfer [13,14]. Mesoporous carbon aerogels, a 3-D network structure of interconnected nanosized primary particles, are considered to be a preferable support. These materials have a unique porous structure including well-developed and controlled interparticle mesopores and intraparticle micropores, huge pore volume and large specific surface area. Moreover, the carbon aerogels have stable physical property under high temperature, and they can be formed into various shapes and can be used without any further forming treatment, making these materials better attractive as a catalyst [15,16]. Iron-based sorbent has been used favorably because of its high performance in capacity and reactivity and regeneration. What's more, iron-based are cheap and abundant in comparison with other metal-based sorbents. Iron-based carbon aerogels adsorbent [17–20] perform high stability at high temperature and have high desulfurization performance. Being incorporated into the structure of carbon aerogels through direct synthesis, the iron or iron oxides can disperse uniformly and perform much better in the removal of $H_2S$ from hot coal gas.

In this work, we provided the new synthetic strategy with an effective method to fix the highly dispersed Fe nanoparticles into the support carbon aerogels skeleton and researched Fe NPs sorbent $H_2S$-removal ability in a fixed-bed reactor within the 500–650 °C range. And the highly dispersed Fe nanoparticles were embedded into the carbon aerogels, showing excellent stability, high sulfur capacity and high desulfurization efficiency at the presence of reducing gas CO and $H_2$. The structural features of the sorbent were assessed by X-ray diffraction (XRD) and high resolution scanning electron microscopy (HRSEM), high resolution transmission electron microscopy (HRTEM), $H_2$ temperature-programmed reduction ($H_2$-TPR), X-ray photoelectron spectroscopy (XPS), and Thermal gravity analysis (TG), their textural properties were investigated by $N_2$ adsorption. This work will propose the traits of novel desulfurizer and explore the potential of this kind of structure being used as adsorbent.

## 2. Experimental

### 2.1. Sorbent preparation and characterization

Carbon aerogels were prepared by aqueous sol–gel polymerization of resorcinol (R) and formaldehyde (F) using sodium carbonate as a basic sorbent (C) [21]. In a typical procedure, 10 g of resorcinol and 14.63 g of formaldehyde (37 wt%) were dissolved in 100 mL distilled water, and the molar ratio of R to C(R/C) was varied. Firstly, the RF solutions were stirred at 30 °C for 2 h and the mixture was cured at 30 °C for one day, 50 °C for one day and poured into sealed glass vials to prevent the evaporation of water during gelation in a water bath at 80 °C for 3 days. Secondly, the as-prepared hydrogels have structures filled with water. To remove water from their structures, the gels were solvent exchanged by immersing in alcohol for three days prior to the freeze drying. Thirdly, carbon aerogels were obtained by pyrolysis of organic aerogels at 950 °C for 3 h with a heating rate of 5 °C/min under the nitrogen atmosphere. The as-prepared carbon aerogels are denoted as Cx, where x represents concentration of the catalysts (mole ratio of R/C). For example, when the mole ratio of R/C is 700, the prepared carbon aerogel is referred as C700. The Fe nanoparticles supported on carbon aerogels were prepared by wet impregnation of aqueous solutions of $Fe(NO_3)_3$. The mixture were dissolved in 20 ml deionized water and stirred for 6 h until a monolith was formed. Then the mixture was dried at 90 °C for 12 h in the oven and calcined in a furnace under nitrogen atmosphere by ramping from room temperature to 400 °C at a heating rate of 1 °C/min and then the temperature was increased up to 800 °C at a heating rate of 5 °C/min and remained at the same temperature for 2 h, mesoporous carbon aerogels could well reduce $Fe^{III}$ ion to $Fe^0$ at 800 °C. Finally, the 50%Fe/C700 desulfurizers (50 wt%Fe) were prepared. Characterization techniques were shown in Supporting Information.

### 2.2. Activity tests of the impregnated carbon aerogels for $H_2S$ removal

The performance of the as-prepared desulfurizers was evaluated in a fixed-bed reactor. Approximately 0.2 g desulfurizer was packed in a glass tube with the diameter of 16 mm and the height of 800 mm. A simulated mixed gas with a composition of 0.2% $H_2S$, 10–30% $H_2$, 10–20% CO, and $N_2$ as balance was passed through the column of the sorbents with a flow rate of 100 mL/min and sulfidation experiment was conducted at weight hourly space velocity (WHSV) of 30,000 $mL{\cdot}h^{-1}{\cdot}g^{-1}$. The gases were controlled by mass flow controllers and then flowed through a vertically oriented quartz tube reactor. The breakthrough concentration of $H_2S$ was monitored using a gas chromatograph. When the concentration excesses 100ppmv, it could be considered the moment of the bed breakthrough. After performance optimization, the 50%Fe/C700 desulfurizer was found to be the best and was selected for successive sulfidation-regeneration investigation. The regeneration of used desulfurizer was conducted at 700 °C in a 50% $SO_2/N_2$ as balance gas flow. The regeneration experiments were finished when the $SO_2$ concentration reached the content of feed gas. $H_2S$ or $SO_2$ in the exit gas was measured by a gas chromatograph (Fuli Analytical Instrument Co., Ltd, GC9790IIH-2, China), equipped with a thermal conductivity detector (TCD) and a flame photometric detector (FPD) for low concentrations of $H_2S$ or $SO_2$ with sensitivity lower than 5 ppm or 50 ppm, respectively.

### 2.3. $H_2S$ breakthrough capacity

In the present study, the performance of sulfur-removal was evaluated based on sulfur capacity of the desulfurizers. The