



# Ultrasonic-assisted preparation of highly reactive Fe–Zn sorbents supported on activated-char for desulfurization of COG



Jinxiao Dou<sup>a</sup>, Jianglong Yu<sup>a,b,\*</sup>, Arash Tahmasebi<sup>a</sup>, Fengkui Yin<sup>a</sup>, Sushil Gupta<sup>c</sup>, Xianchun Li<sup>a</sup>, John Lucas<sup>b</sup>, Chuan Na<sup>a</sup>, Terry Wall<sup>b</sup>

<sup>a</sup> Key Laboratory for Advanced Coal and Coking Technology of Liaoning Province, School of Chemical Engineering, University of Science and Technology Liaoning, Anshan 114051, China

<sup>b</sup> Chemical Engineering, University of Newcastle, Callaghan, NSW 2308, Australia

<sup>c</sup> SMART@UNSW, School of Materials Science & Engineering, University of New South Wales, Sydney 2052, Australia

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## ABSTRACT

The desulfurization properties of Fe–Zn sorbent prepared by impregnating Fe and Zn into lignite char via ultrasonic-assisted impregnation (UAI) were investigated in comparison with the mechanical stirring (MS) method. The sulfidation experiments were carried out using a fixed-bed quartz reactor under ambient pressure. The amounts of metals loaded into char were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES). The crystalline phases and chemical structure of sorbents before and after sulfidation were characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR), respectively. The morphology of sorbents was analyzed by using scanning electron microscope (SEM) with an energy dispersive X-ray (EDX) auxiliary. The experimental results showed that metal oxides as the active components were evenly dispersed on char as nanoparticles. The impregnation of active components was significantly improved by the ultrasonic-assisted impregnation method. When sorbents were prepared by ultrasonic-assisted impregnation, the metal oxide particles became smaller and more evenly dispersed on the char matrix which resulted in higher desulfurization efficiency and sulfur uptake capacity of the sorbents. The BET results showed that the physical properties of sorbents (surface area and pore volume) significantly improved when prepared by UAI method compared to MS method. The sulfidation temperature had a significant effect on desulfurization performance of char supported sorbents. The Fe:Zn molar ratio of 2:1, and impregnation time of 9 h were suggested as the optimal preparation conditions during ultrasonic-assisted impregnation.

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## 1. Introduction

Coke oven gas (COG) is the by-product of the coke making process. COG cleaning is attracting increased attention as a part of the development of efficient and environmentally friendly coal-based energy technology [1]. COG can be used for various applications including production of hydrogen, ether and dimethyl ether (DME) [2]. The use of membrane technology can lead to syngas production through the partial oxidation of COG [3]. The syngas produced from COG can be used to produce organic products, such as methanol [4]. Catalytic hydrogenation of CO and CO<sub>2</sub> can also be used to produce CH<sub>3</sub>OH [5]. However, the presence of sulfur as H<sub>2</sub>S, COS and CS<sub>2</sub> in COG is one of the major technical barriers for effective utilization of COG, due to potential air pollution, equipment corrosion, and catalyst poisoning issues during the subsequent processes such as combustion and synthesis processes. Therefore, the development of efficient desulfurization methods is of

primary importance for improving the economic and environmental sustainability of coke-making industry [6,7].

Sulfur containing impurities in COG, mainly H<sub>2</sub>S and COS, can be removed using either wet or dry desulfurization processes. Wet desulfurization technology is well established in the coke making industry and regarded as a sufficiently developed separation process [2]. However, some issues such as high operation cost, high water consumption, waste water treatment, and poisoning of the catalyst are the disadvantages of the wet process. Dry desulfurization using carbon-based sorbents under the medium temperature range of 300–550 °C has the advantages of low capital cost, simplified process, low operating costs, energy saving, no water consumption, and high desulfurization efficiency. Moreover, dry desulfurization has the potential to simultaneously remove impurities containing both sulfur and nitrogen. Recently, hot coal gas desulfurization using lignite char supported sorbents has been reported by the authors [8–11].

Preparation of novel sorbents with high desulfurization performance is essential to achieve a higher sulfur removal, and to improve the efficiency of coal utilization processes. Various desulfurization

\* Corresponding author. Tel.: +61 2 40333902.

E-mail address: [jianglong.yu@newcastle.edu.au](mailto:jianglong.yu@newcastle.edu.au) (J. Yu).

sorbents, such as zinc oxide, iron oxide, manganese oxide, copper oxide, calcium oxide, and mixed metal oxides have been investigated for hot coal gas desulfurization [12–18]. Zinc oxide (ZnO) with a high equilibrium constant has a good precision and has shown stable and reliable performance in H<sub>2</sub>S removal [19]. Iron oxide sorbents have also been widely used for removing H<sub>2</sub>S, SO<sub>x</sub> and NO<sub>x</sub> from coal based gas streams due to their advantages of high sulfur capacity, high reactivity, low cost, and simple operation [8,20]. The desulfurization properties of iron based sorbents could be further improved by addition of cobalt, molybdenum and zinc compounds. Zinc ferrite (ZnFe<sub>2</sub>O<sub>4</sub>), which possesses the properties of both Zn and Fe based sorbents, has been reported as a highly reactive component for desulfurization [21–26]. Lignite char supported Fe-based sorbents can be used for hot coal gas and coke oven gas desulfurization [8–11].

Properties of sorbents are dependent upon their method of the preparation. The ultrasonic assisted impregnation (UAI) method has recently gained much attention as a promising crystallization method [27,28]. The UAI method has diverse applications in chemical processes including organic synthesis, catalytic reactions, and environmental and engineering science [23,27–29]. High dispersion of active components on the carrier surface can be achieved by using this technique. Mi et al. [23] prepared activated semi-coke supported ZnFe<sub>2</sub>O<sub>4</sub> sorbents under UAI. High dispersion of ZnFe<sub>2</sub>O<sub>4</sub> on activated semi-coke was achieved through UAI. A combination of ZnFe<sub>2</sub>O<sub>4</sub> and activated semi-coke leads to an increased porosity and a large specific surface area and resulting a higher sulfur capacity compared to unsupported ZnFe<sub>2</sub>O<sub>4</sub> sorbent. As mentioned above, the use of UAI in sorbent preparation is a promising method, through which the uniform dispersion of nano-sized particles on catalyst support with higher level of metal loading can be achieved. One advantage of this process is that it does not require stringent conditions such as high temperatures and pressures during the preparation process.

In our previous study, mechanical stirring (MS) method was used for the preparation of sorbents [30] during which the dispersion of active components was a concern. In this study, ultrasonic assisted irradiation method was used for impregnation of Fe–Zn active components on char support. The sulfidation properties of lignite char supported Fe–Zn sorbents prepared by two different methods were systematically examined.

## 2. Experimental

### 2.1. Preparation of sorbents

Shenhua lignite from the Inner Mongolia region in China was used in this study. The results of the ultimate analysis of the lignite sample are as follows: moisture content, 19.96%, volatile matter, 30.89%; fixed carbon, 45.12%; and ash content, 4.03%.

The coal was crushed and sieved to 75–125 μm particle size and then dried under nitrogen at 105 °C. The coal samples were then acid-washed using 0.4 N HCl aqueous solution for 12 h, which were assigned as AW coal. The AW coal was mixed with ferric nitrate and/or zinc nitrate solution (Sinopharm Chemical Reagent Co. Ltd) with a mass ratio of AW coal to nitrate of 10:1. In the case of co-precipitation of Zn and Fe, the molar ratios of ferric nitrate to zinc nitrate were 3:1, 2:1 and 1:1 respectively. The impregnation was performed by using an ultrasonic apparatus (Kunshan, KQ5200DE, 100KW and 20KHZ). The three samples were first impregnated under MS or UAI at 50 °C inside the water bath of the apparatus. The MS impregnation time was 9 h, but the UAI impregnation time was varied between 3 and 12 h at 3 hour intervals in order to investigate the effect of the impregnation time on desulfurization performance. Titration of the slurry was done using NH<sub>3</sub>·H<sub>2</sub>O aqueous solution. MS or UAI was performed at 50 °C for 1 h. The slurry was then filtered and washed with de-ionized water. The samples were dried at 105 °C under nitrogen. Pyrolysis and gasification experiments were carried out in a vertical fixed-bed tubular quartz reactor with an

internal diameter of 2.0 cm heated by an electric furnace. About 2.0 g of sample was used and before the start of each experiment, the reactor was purged with N<sub>2</sub> at 100 ml/min flow rate for 5 min to ensure that an inlet atmosphere is achieved. When the furnace reached to the desired temperature (700 °C), the reactor was inserted into the furnace and heated for 15 min. Steam was then introduced (15 % vol. balanced with nitrogen) for 30 min. After the gasification, the reactor was taken out of furnace and cooled down at room temperature. The sorbents were assigned as FZ1, FZ2, and FZ3, respectively, and their composition is presented in Table 1.

### 2.2. Characterization of sorbents

The amounts of loaded metals were measured by an Inductively Coupled Plasma Atomic Emission Spectrometry (Beijing Haiguang WLY100-1 ICP-AES). The crystalline phases associated with the sorbents were determined by using powder X-ray diffraction (XRD 7000, Shimadzu) with Cu-Kα radiation. The applied current and voltage were 30 mA and 40 kV, respectively. Diffraction patterns were recorded from 10° to 80° with a scan rate of 3°/min.

A Thermo Fisher Nicolet IS5 mid FTIR Spectrometer was used to study the chemical structure of the sorbents. Prior to FTIR analysis, KBr and samples were dried in the vacuum oven for 12 h to ensure that there was no moisture to affect the results. The pellets were prepared by grinding 1 mg of sorbent with 150 mg of KBr. Infrared spectra of the sorbent samples were obtained for the 4000–400 cm<sup>-1</sup> region. The FTIR measurements were repeated 3 times and the results presented here are the average of these measurements.

The surface morphology of the sorbents before and after sulfidation was investigated by using a scanning electron microscope (SEM) (Hitachi FESEM 3400) with energy dispersive spectroscopy (EDS) auxiliary.

The BET (Brunauer–Emmett–Teller) analysis of the sorbents was carried out in pore size analyzer (ASAP2020) using N<sub>2</sub> gas adsorption method. Specific surface area and pore volume were calculated based on N<sub>2</sub> adsorption isotherm and Barrett–Joyner–Halenda (BJH) method was used to determine the pore size distribution.

### 2.3. Sulfidation experiments

Sulfidation experiments were carried out by using a fixed-bed quartz reactor in an electrically heated furnace at ambient pressure and at a space velocity of 1000 h<sup>-1</sup>. The simulated COG comprised of 7.38% CO, 2.65% CO<sub>2</sub>, 0.345% H<sub>2</sub>S, 0.014% COS, 26.55% CH<sub>4</sub>, 3.97% N<sub>2</sub> and balanced by H<sub>2</sub>. The feed gases were supplied from gas cylinders and the gas flow rates were controlled by mass flow controllers. The vertical quartz reactor with an inner diameter of 10 mm was used. Approximately 1.1 g (3 ml) of sorbent was placed inside the reactor. Analysis of the outlet and inlet gases was carried out by gas chromatographer (GC-9890B, Shanghai Linghua Equipment) using a flame photometric detector (FPD) for compounds with low sulfur concentration; and a thermal conductivity detector (TCD) for compounds with high sulfur concentration. Details of the experimental setup and procedure have been given elsewhere [10].

**Table 1**  
Compositions and sulfur capacity of different sorbents prepared by mechanical stirring and ultrasonic-assisted impregnation method.

Methods	Sample	Fe content (%, wt.)	Zn content (%, wt.)	Sulfur capacity (g S per 100 g sorbent)
MS	FZ2	10.8	4.0	8.31
UAI	FZ1	13.8	7.6	14.65
	FZ2	14.3	5.6	13.91
	FZ3	13.4	5.1	12.10

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