



Ordered mesoporous Zn-based supported sorbent synthesized by a new method for high-efficiency desulfurization of hot coal gas

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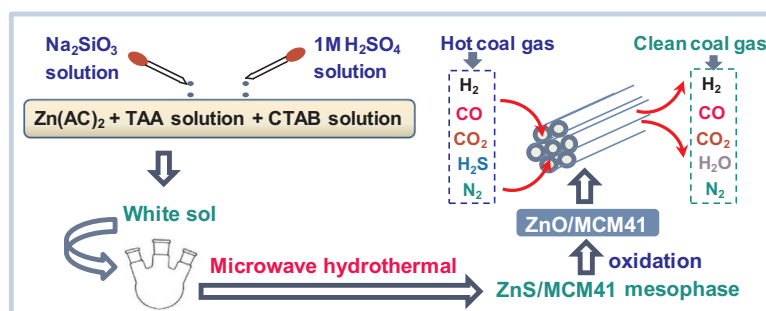
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HIGHLIGHTS

- A new approach was proposed for the preparation of the Zn-based sorbents.
- The sorbent show ordered mesoporous structure before and after desulfurization.
- The optimized sorbents exhibits superior and stable desulfurization ability.
- Zn_2SiO_4 in the sorbents could react with H_2S during the desulfurization process.
- Regeneration is highly effective to restore the pore structure of sorbents.

GRAPHICAL ABSTRACT



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ABSTRACT

A new approach (microwave-hydrothermal plus oxidation) was proposed for the preparation of the Zn-based sorbents supported on the ordered mesoporous Si-based material. The hydrothermal synthesis and oxidation conditions of the sorbent precursor (ZnS/MCM41 mesophas) with $\text{Zn}(\text{AC})_2$ and thioacetamide (TAA) as the Zn and S sources, respectively, were optimized. The sorbents were evaluated in a fixed bed using the simulate gas of 2000 ppm H_2S , 39% H_2 , 27% CO , 12% CO_2 , and N_2 as balance gas. The structure of the sorbents was characterized by means of XRD, N_2 adsorption, SEM, EDX, and TEM analysis. The results indicate that the optimal microwave-hydrothermal conditions are 400 W, 2.5 h, and 1:3 (the mole ratio of the $\text{Zn}(\text{AC})_2$ to TAA). The oxidation of ZnS in the sorbent precursor to ZnO is invalid at 550 °C due to unfavorable reaction kinetics. Both the fresh and used sorbents show ordered hexagonal mesoporous structure. It is confirmed that Zn_2SiO_4 present in the fresh and regenerated sorbents could be consumed during the desulfurization process via the reaction ($\text{Zn}_2\text{SiO}_4 + 2\text{H}_2\text{S} \rightarrow 2\text{ZnS} + \text{SiO}_2 + 2\text{H}_2\text{O}$), giving a positive effect on the desulfurization of the sorbents. The optimized Zn-based mesoporous sorbent (actual Zn content: 20.3%) exhibits superior (high breakthrough sulfur capacity: 5.4–5.7%) and stable desulfurization ability during five sulfidation/regeneration cycles. In addition, sulfidation reaction only leads to low-degree plugging of the pore structure of the regenerated sorbents, and the regeneration reaction could restore (at least mostly) the aforementioned changes in the pore properties.

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1. Introduction

Coal resources could be utilized by different ways, such as gasification, combustion, liquefaction, coking, and so on [1,2]. The gasification of coal is the key technique for the advanced technologies (e.g. Integrated Gasification Combined Cycle technology) for electric power generation using coal gas [2]. However, H_2S is produced as the main gaseous sulfur-containing compounds in the gasification gas [3,4]. The concentration of H_2S in the coal gas must be lower than 20 ppm in order to avoid the corrosion of gas turbines used in the technique of Integrated Gasification Combined Cycle (IGCC) [3,5]. Desulfurization at 350–550 °C is recommended if the overall economy of the IGCC process is taken into consideration [6].

Metal oxides (MnO_2 , Fe_2O_3 , ZnO , etc.) are widely used as the sorbents for the H_2S removal of the hot coal gas [7–17]. MnO_2 exhibits higher initial sulfidation rate than Fe_2O_3 and ZnO according to the kinetic studies [11], while higher equilibrium concentration of H_2S is observed when Mn-based sorbents are used for desulfurization at high temperatures [3,11]. Although iron oxide is low-cost and has higher sulfur capacity [8,16], the sulfidation reaction thermodynamics of Fe_2O_3 is less favorable than that of ZnO [3]. ZnO is the most widely used sorbents for the desulfurization of the natural gas feedstock [3,17], and the highly efficient removal of H_2S in the coal-derived gas from several thousand ppm down to ca. 1 ppm could be achieved [3]. However, the reduction of ZnO at high temperatures under the atmosphere of the coal gas is inevitable, leading a decline in the desulfurization activity [3]. A number of studies on desulfurization using ZnO stabilized by TiO_2 have been reported [18], but the decrease in the sulfidation reactivity is also accompanied. To date, it is challenging to develop Zn-based sorbents with good thermal stability and long-term desulfurization ability.

The porous metal oxide (ZnO as an example) sorbent particle can be seen as the assemblage of numerous nonporous grains with small size, and pores are surrounding these nonporous grains [19,20]. The reactant H_2S and product H_2O can diffuse through the pores to the surface of the grains (or the gas phase) [17,21]. As shown in Fig. 1a, the ZnO particle would expand and become more denser during the desulfurization process, which is attributed to the replacement of O^{2-} (ionic radii: 0.140 nm) by S^{2-} (ionic radii: 0.184 nm) leading to greater grain size in the resulting metal sulfide. The expansion of the particles would result in an increase in the press drop of the sorbent bed, unfavorable for the stable operation of the desulfurization setup. A large number of opened pores would also become closed, which has a negative effect on the following regeneration of used sorbents due to the difficulty of the contact between O_2 and ZnS . In addition, the sorbents could crack in the case of excessive expansion. In our previous study [22], a route

(Route-A) for the preparation of the sorbents was proposed in order to solve the problems mentioned for the conventional method. As shown in Fig. 1b, the sorbent precursor (ZnS) was firstly prepared, then the precursor undergoes the oxidation treatment, and the resulting fresh ZnO sorbent is obtained. The pore structure (Fig. 1b) of the sorbent precursor (ZnS) is similar to that of the fresh sorbent depicted in Fig. 1a. Oxidation treatment results in more porous structure of the resulting fresh sorbent. More porous structure could supply larger space for the expansion of grains caused by the replacement of O^{2-} by S^{2-} . Therefore, no expansion of the sorbent pellet occurs theoretically, beneficial for the smooth running of the desulfurization process. Furthermore, for the fresh sorbent (Fig. 1b), the formation of closed pore structure caused by sulfidation reaction is less significant compared to the conventional method. It is beneficial for the subsequent regeneration of the used sorbents. Unfortunately, the sorbent (ZnO supported on the dense red clay) prepared via the Route-A (Fig. 1b) exhibits poor ability of adsorbing H_2S due to very small surface area ($< 16\text{ m}^2\text{ g}^{-1}$) and pore volume ($< 0.05\text{ m}^3\text{ g}^{-1}$) [22]. Furthermore, there are breakages and cracks of the sorbents due to significant sintering corresponding to uncontrollable growth of the grains of ZnO and ZnS [22]. Therefore, using a porous supporter and inhibiting the grain sintering of sorbent is crucial for using Route-A to synthesize the sorbents.

Compared to the unsupported sorbents, the porous supporter [9,10,12–17], especially the ordered mesoporous material (MCM41 [17], KIT-6 [23], etc.), can supply larger pore volumes for the dispersion of metal oxide and diffusion of the gaseous reactant (or product), enhancing the desulfurization activity of the sorbents. More importantly, the anti-sintering properties of the metal oxide can be improved via the space confinement of mesoporous pores [24,25], which is ascribed to the fact that the metal oxide (or metal sulfide) grains can be isolated by the pore channel, preventing the mitigation and aggregation of the grains. Gabaldon [24] claimed that the ordered Si-based mesoporous materials with one-dimensional channels are more effective in stabilize the nano-metal particles than those with ordered 3D mesostructure. We have synthesized the MCM41 (with ordered 1D mesostructure) supported ZnO by the one-step hydrothermal way [17] and the sorbents shows good desulfurization/regeneration stability during multiple sulfidation/regeneration cycles [17]. However, a further improvement is necessary in order to obtain a higher adsorption capacity and desulfurization efficiency. In addition, the conventional hydrothermal treatment also takes long time (48 h) [17].

Herein, a novel method for preparing the sorbents was proposed to make use of the advantages of the Route-A and ordered mesoporous materials. Specifically, the MCM41 mesophase supported ZnS as the sorbent precursor was first synthesized via the hydrothermal method. The precursor was then oxidized to obtain the mesoporous Zn-based sorbent. The effect of the Zn source (or S source) and synthesis conditions on the structure of sorbent precursor was investigated. The influence of the oxidation treatment on the structure of the fresh sorbent was also studied. The desulfurization performance of the sorbents with different Zn contents was evaluated. The successive sulfidation-regeneration behavior was also investigated.

2. Experimental section

2.1. Synthesis of sorbent precursor

A typical synthesis procedure was as follows: First, 4.04 g of cetyltrimethyl ammonium bromide (CTAB) was dissolved into 30 mL of deionized water. Then the aqueous solution containing certain amount of zinc (Zn) source and sulfur (S) source was added to the aforementioned solution under rapid stirring. Once the white sol was formed, the Na_2SiO_3 solution (15.8 g of Na_2SiO_3 and 30 mL of H_2O) was added dropwise with continuous stirring. After the pH of the resulting solution was adjusted to 10 with 1 mol L^{-1} H_2SO_4 solution, a further stirring for 5 h was carried out. The light-gray sol was then obtained. The molar

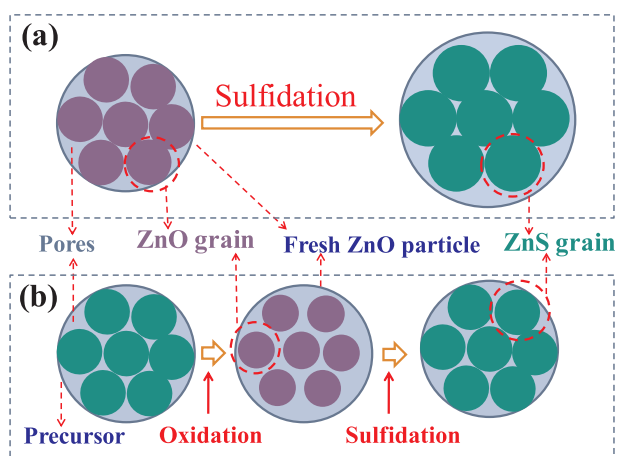


Fig. 1. Schematic diagrams of ZnO sorbent particle prepared by conventional method (a) and Route-A (b).

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