



Highly stable and regenerable Mn-based/SBA-15 sorbents for desulfurization of hot coal gas

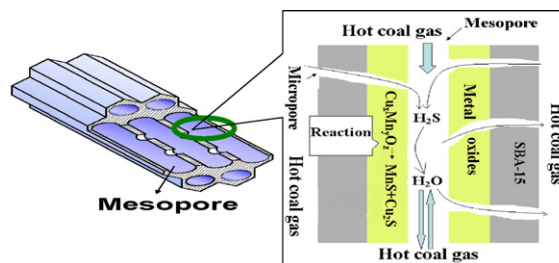
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HIGHLIGHTS

- ▶ A series of mesoporous $\text{Cu}_x\text{Mn}_y\text{O}_z/\text{SBA-15}$ sorbents were fabricated for hot coal gas desulfurization.
- ▶ $1\text{Cu}9\text{Mn}/\text{SBA-15}$ sorbent with high breakthrough sulfur capacity is high stable and regenerable.
- ▶ Utilization of SBA-15 constrained the sintering and pulverization of sorbents.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of mesoporous $x\text{Cu}y\text{Mn}/\text{SBA-15}$ sorbents with different Cu/Mn atomic ratios were prepared by wet impregnation method and their desulfurization performance in hot coal gas was investigated in a fixed-bed quartz reactor in the range of 700–850 °C. The successive nine desulfurization–regeneration cycles at 800 °C revealed that $1\text{Cu}9\text{Mn}/\text{SBA-15}$ presented high performance with durable regeneration ability due to the high dispersion of Mn_2O_3 particles incorporated with a certain amount of copper oxides. The breakthrough sulfur capacity of $1\text{Cu}9\text{Mn}/\text{SBA-15}$ observed 800 °C is 13.8 g S/100 g sorbents, which is remarkably higher than these of 40 wt% $\text{LaFeO}_3/\text{SBA-15}$ (4.8 g S/100 g sorbents) and 50 wt% $\text{LaFe}_2\text{O}_x/\text{MCM-41}$ (5.58 g S/100 g sorbents) used only at 500–550 °C. This suggested that the loading of Mn_2O_3 active species with high thermal stability to SBA-15 support significantly increased sulfur capacity at relatively higher sulfidation temperature. The fresh and used $x\text{Cu}y\text{Mn}/\text{SBA-15}$ sorbents were characterized by means of BET, XRD, XPS, XAES, TG/DSC and HRTEM techniques, confirmed that the structure of the sorbents remained intact before and after hot coal gas desulfurization.

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1. Introduction

In recent decades, integrated gasification combined cycle (IGCC) [1] technology and solid oxide fuel cell (SOFC) unit [2] were developed for high effective utilization of coal. Coal-derived gas, containing a certain concentration of sulfur compounds, nitrogen oxides, etc., cannot be applied in generating electricity directly. Sulfur compounds in hot coal gas not only result in the corrosion of pipe line and turbine, but also induce air pollution. So it is required to remove the sulfur compound from coal gas. Recently,

conventional methods, such as wet limestone [3] and ammonia scrubber desulfurization [4] are unfavorable for reducing operation capital from the economic point of view. Therefore, the oxides of Fe, Zn, Ca, Mg, and Co as regenerative sorbents for hot coal gas desulfurization are studied extensively in recent years [5–13]. However, sintering, mechanical pulverization and reductive properties at temperature higher than 700 °C limited the application of aforementioned metal oxides. From the economic viewpoints, it is required to increase the desulfurization temperature since the generation and combustion of coal-derived gas is in the range of 750–1000 °C. Therefore, the studies on metal oxide sorbents which can be used at high temperature (>600 °C) have attracted considerable attention of scientific researchers in the world.

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According to the report of Westmoreland and Harrison [5], manganese oxides are stable in the form of MnO at reductive atmosphere between 400 and 1000 °C and have a superior initial desulfurization rate compared to oxides of V, Ca, and Zn [6]. Similarly, Slimane and Hepworth [14,15] also found that manganese-based sorbents presented high initial sorption rate, high sulfur capacity and good regenerative ability during hot coal gas desulfurization at 700–1000 °C but with high H₂S equilibrium concentration (around 150 ppmv). Therefore, a variety of oxides, such as zinc oxide [16–19], iron oxides [18,20–22], copper oxides [19,21,23,24], and vanadium oxides [25,26] were incorporated into manganese oxides in order to increase the H₂S removal efficiency. However, the application of zinc and ferric oxides is limited to a maximum temperature of 600 °C due to zinc evaporation and the reduction of ferric oxides at reductive atmosphere. The incorporation of copper oxides can enhance the dispersion of manganese oxides and improve the desulfurization performance of Mn-based adsorbents with H₂S pre-breakthrough concentration of 50 ppmv [19,21,23,24]. Furthermore, copper oxides can also maintain its desulfurization ability at above 800 °C [5,27]. Therefore, the development of sorbents is focusing on the Cu and Mn mixed oxides with high sulfur capacity in the range of higher than 600 °C.

In addition, in order to resolve the scientific problems, such as sintering, low utilization of active components and mechanical attrition of sorbents, the metal oxides supported on zeolite [28,29], TiO₂ [30] and γ -Al₂O₃ [18] indeed increased the stability of sorbents but decreased sulfur capacity. The decline of the surface area and porosity are unavoidable during successive desulfurization–regeneration cycles. Considering that SBA-15 and MCM-41 presented good thermal stability with high surface area and large pore volumes and were widely used in many domains [31–34], we reported La_xMe_yO_z (Me = Fe, Co, Zn)/MCM-41 or SBA-15 desulfurization of hot coal gas in middle temperature (550–600 °C) [7,8], which showed good regeneration stability and diffusion rate of gas. Furthermore, the CuO/SBA-15 or MCM-41 [35–37] also exhibited excellent performance for hot coal gas desulfurization. Therefore, in order to fabricate sorbents with high sulfur capacity and renewable ability at high temperature, a series of xCu_yMn/SBA-15 were prepared due to the relative high hydrothermal stability of SBA-15 and their desulfurization activities were investigated. The properties of fresh and used xCu_yMn/SBA-15 sorbents were characterized by means of nitrogen adsorption (BET), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy (HRTEM) and thermogravimetry/differential scanning calorimetry (TG/DSC).

2. Experimental

2.1. Preparation of SBA-15 and sorbents

SBA-15 was prepared according to method reported by Zhao et al. [38]. First, 4 g of Pluronic P123 (Aldrich Co. MW 5800) was dissolved in 150 mL HCl (1.6 mol/L) with stirring at 40 °C. 9 mL of TEOS was added dropwise with consistently stirring for another 20 h. The obtained mixture was transferred into the Teflon-lined stainless steel autoclave and treated at 100 °C for 24 h. Then, the white precipitate was filtered, washed with deionized water (DW), dried at room temperature (RT) for two days and finally calcined at 550 °C for 5 h in flowing air (500 mL/min).

All sorbents were prepared by a sol–gel method. Taking the preparation of 1Cu9Mn/SBA-15 sorbent as an example, 10.50 g of 50 wt%Mn(NO₃)₂ solution and 0.79 g of Cu(NO₃)₂·3H₂O were dissolved in 25 mL DW followed by addition of 5 mL HNO₃ (6 mol/L) in the solution. After the addition of citric acid with molar amount of 1.5 times that of total metal ions, 2.5 g of as-prepared SBA-15

was added to aforementioned solution. The mixture was kept at 60 °C with constant stirring until it became a viscous gel and then dried at RT for two days. Finally, the samples were calcined in air at 550 °C for 6 h. The obtained xCu_yMn/SBA-15 sorbents with different Cu/Mn atomic ratios are denoted as 5Cu5Mn/SBA-15, 3Cu7Mn/SBA-15, 1Cu9Mn/SBA-15 and 10Mn/SBA-15, respectively (the numbers before Cu and Mn represent the molar number in mixed metal oxides). The amount supported CuO and Mn₂O₃ in SBA-15 is 50 wt%.

2.2. Characterization of sorbents

Nitrogen adsorption isotherms of SBA-15, fresh and used sorbents were investigated at 77 K in a homemade system [39]. Prior to analysis, the sorbents were treated in vacuum at 200 °C for 2 h. BET surface area, pore volume and average pore diameter were calculated using adsorption isotherm while pore size distribution was estimated by Barrett, Joyner and Halenda (BJH) method [39]. The structures of fresh and used sorbents were investigated by HRTEM on a Tecnai G2 F20 electron microscopy operated at 200 kV.

The small-angle XRD patterns were recorded with a Rigaku D/max 2500 v/pc Automatic Diffractometer equipped with Ni filtered Cu K α radiation (20 kV, 30 mA). Wide-angle XRD patterns (10–70°) were measured with a PANalytical Automatic Diffractometer using Ni-filtered Cu K α radiation (λ = 0.15406 nm) at settings of 40 kV and 50 mA.

The XPS signals were obtained with a PHI-1600 ESCA spectrometer equipped with Mg K α X-ray source (1253.6 eV). The binding energies (BEs) of the samples were calibrated with the contaminant C 1s line (284.6 eV). The Cu 2p XPS and Mn LMM Auger spectra were fitted by 80% Gaussian–Lorentzian method using XPSPEAK software (version 4.1, Chinese University of Hong Kong) due to poor signal-to-noise ratios. TG/DSC analysis for 1Cu9Mn/SBA-15 precursor and 1Cu9Mn/SBA-15 used at 800 °C was carried out in air. Approximately 10 mg of sample was heated from 30 to 1100 °C at the rate of 10 °C/min and the data was obtained on a STA 409 PC/PG model instruments.

2.3. Performance of sorbents for hot coal gas desulfurization

The desulfurization performance of the sorbents for hot coal gas was tested in a fixed-bed micro-reactor. The experimental set up was described in details elsewhere [8]. The inlet stream was controlled by mass flow controllers (D07-7B/ZM, Beijing Sevenstar Electronics Co., Ltd., China) at 165 mL/min consisted of 72% N₂, 10.5% H₂, 17.1% CO and 0.33% H₂S. Approximately 0.5 g sorbent was packed into a quartz reactor (i.d. 10 mm) and the reaction temperature was controlled by a K-type thermal couple. The sorbents were first heated to the reaction temperature in N₂ at the rate of 10 °C/min and the simulated coal gas was then introduced to the reactor for desulfurization. The concentration of H₂S in inlet and outlet gas was analyzed by iodometry method to obtain H₂S breakthrough curve and breakthrough sulfur capacity (the outlet H₂S concentration of more than 100 ppmv is defined as the breakthrough point). The performance of sorbents was evaluated by the effective sulfur capacity (SC) according to Eq. (1):

$$SC = WHSV \times \left[\frac{M}{V_m} \times \int (C_{in} - C_{out}) dt \right] \times 10^{-4} \quad (1)$$

where SC represents the effective sulfur capacity (g S/100 g sorbents); WHSV is weight hour space velocity (L/(h g)); M is molecular weight of sulfur (g/mol); V_m is the molar volume of H₂S at standard pressure and 25 °C (24.5 L/mol); C_{in} and C_{out} are the inlet and outlet concentration (ppmv) of H₂S, respectively; t is the breakthrough time for desulfurization (h).

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