CeO$_2$–MnO$_x$/ZSM-5 sorbents for H$_2$S removal at high temperature

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HIGHLIGHTS

- The sulfidation activity of CeO$_2$ was significantly enhanced by addition of Mn.
- 5Ce5Mn/ZSM-5 sorbent had the highest sulfur capacity of 7653.1 μmol S/g.
- H$_2$ repressed sulfur removal and CO had a little impact on sulfidation reaction.

GRAPHICAL ABSTRACT
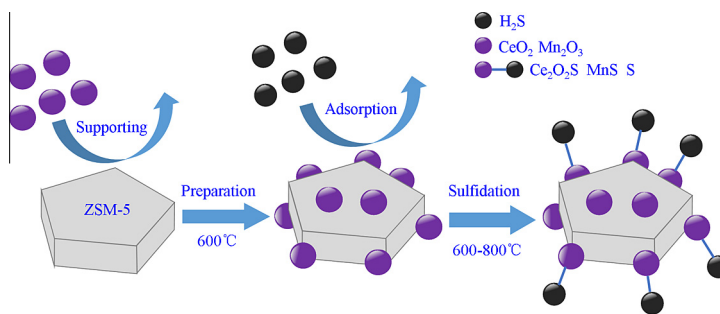
ABSTRACT

xCeyMn/ZSM-5 sorbents were prepared using sol–gel method and employed for H$_2$S removal in the temperature range of 600–800 °C. The sorbents exhibited high performance in sulfur removal due to the cooperative effect of CeO$_2$ and MnO$_x$. The presence of H$_2$ was unfavorable for sulfidation and obviously shortened the breakthrough time and reduced the sulfur capacity. However, the existence of CO had little impact on the sulfur-removal performance. The characterization results revealed that the ZSM-5 structure remained intact during preparation and sulfidation process. And active species, such as CeO$_2$ and Mn$_2$O$_3$, were well dispersed on ZSM-5, which would suppress the mechanical disintegration and improve the thermal stability of xCeyMn/ZSM-5.

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1. Introduction

In terms of thermal efficiency and environmental protection, integrated gasification combined cycle (IGCC) power technology was regarded as one of the most promising clean coal technologies [1,2]. The gases from coal gasification process contains large amounts of sulfur, mostly in the form of H$_2$S ($\sim$0.1–1.5 vol%) which would cause severe corrosion of downstream equipments and infringement of emission legislation, therefore, the sulfur compounds need to be removed prior to syngas utilization. The conventional techniques for H$_2$S removal such as wet absorption can only occur at much lower temperature than gasification temperature (>1000 °C). Thus, the hot coal gas ($\sim$800–900 °C) has to be cooled down to ambient temperature for sulfur removal and then heated up to a required temperature for burning in gas turbine [3]. To improve the thermal efficiency and lower the capital costs of IGCC system, solid sorbents, such as Fe$_2$O$_3$ [4], CuO [5], and MnO$_x$ [6], which can adsorb H$_2$S at high temperature, would be a better option for hot coal gas desulphurization.

For the last few decades, much work had been concentrated on binary and ternary oxides for moderate- and high-temperature H$_2$S removal, such as Zn–Mn [7], Cu–Mn [8], Fe–Mn [9], ZnFe$_2$O$_4$ [10] and ZnTiO$_3$ [11]. Recently, cerium, a rare earth element of

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lanthanide series, has received increasing attention due to its prominent oxygen storage capacity and unique redox couple Ce^{3+}/Ce^{4+} under oxidizing and reducing conditions, respectively [12]. Within the redox shift between CeO_2 and Ce_2O_3, labile oxygen vacancies and bulk oxygen species with relatively high mobility can be easily generated, and these are active for oxidation processes [13]. It has been reported that CeO_2 is an attractive sorbent for H_2S removal at high temperature, one of the major advantage of CeO_2 is the formation of elemental sulfur, instead of SO_2, during the regeneration phase [14], because of the fact that the gaseous elemental sulfur could be condensed and sold, which can effectively avoid the problem of ultimate sulfur control associated with the utilization of the zinc-based and ferric-based sorbents [15,16]. The main weakness of CeO_2 by itself in H_2S removal is the lower sulfur capacity as compared to ZnO and CuO sorbents. In recent years, several researchers found that Mn has high sulfur capacity and fast sulfidation rate. Bakker et al. [17] reported that supporting Mn onto γ-Al_2O_3 could increase the utilization of Mn and the desulphurization performance of Mn appeared to be stable during successive sulfidation/regeneration cycles, however, it was not easy to sulfidize fully as $MnAl_2O_4$ formed at reductive atmosphere until 800 °C. Besides, Li et al. [18] found that the intimate combination of CeO_2 and MnO_x could remarkably improve the sulfur capacity and desulphurization precision of sorbents as a result of the deformation of CeO_2 lattice, however, the utilization of γ-Al_2O_3 would reduce the sulfur capacity due to Mn ions dissolution into the γ-Al_2O_3 support. In addition, the specific surface areas and pore volumes of unsupported sorbents are quite small and they are easy to be sintering during preparation and sulfidation processes. To overcome this drawback, many researches have been focused on supporting metal oxides onto high-surface-area mesopore silica materials [19,20]. ZSM-5 as a support or catalyst has been extensively used in the field of NO reduction [21], NO adsorption [22], and petrochemical industry [23,24] because of its high surface area and thermal stability.

In this paper, CeO_2–MnO_x mixed oxides were supported onto ZSM-5 and used for H_2S removal in the temperature range of 600–800 °C. The mechanism of H_2S adsorption on xCeyMn/ZSM-5 were studied via analyzing the characterization data, including effects of sorbent microstructure, sorbent composition, crystalline size, surface area, pore volume, state of active species on the desulphurization performance. The sulfidation tests were then conducted to evaluate the effects of reaction temperature, sorbent composition, H_2 content and CO content on the desulphurization performance.

2. Experimental

2.1. Sorbent preparation and characterization

A series of xCeyMn/ZSM-5 sorbents with 50 wt% ZSM-5 and a specific Mn content of 10, 30, 50, 70, and 90 at% prepared by sol–gel method were denoted as 9Ce1Mn/ZSM-5, 7Ce3Mn/ZSM-5, 5Ce5Mn/ZSM-5, 3Ce7Mn/ZSM-5, and 1Ce9Mn/ZSM-5, respectively. And the numbers before Ce and Mn represented the Ce/Mn molar ratio in the mixed metal oxides. Stoichiometric amounts of cerous nitrate $Ce(NO_3)_3 \cdot 6H_2O$ (AR, Aladdin Reagent, Inc., China) and manganese nitrate $Mn(NO_3)_2 \cdot 4H_2O$ (AR, Aladdin Reagent, Inc., China) were dissolved in 25 mL of nitric acid (~2 mol/L). After the addition of citric acid with a molar amount of 1.5 times that of the total metal ions, ZSM-5 (Catalyst Plant of Nankai University, China) was added to the aforementioned solution. The mixture was kept at 60 °C over a water bath until a viscous gel was generated. Then, the gel was firstly aged at ambient temperature for 3 days, dried at 120 °C for 12 h, and finally calcined at 600 °C for 6 h at a muffle

furnace. Eventually, all sorbents were pressed, ground and sieved through 80–100 meshes [25].

N_2 adsorption/desorption isotherms of ZSM-5, fresh and used sorbents were measured at 77 K in a Beishide 3H-2000PS4 apparatus (Beishide Instrument S&T Co., Ltd, China). Prior to analysis, the sorbent was treated in vacuum at 150 °C for 4 h. Brunauer–Emmett–Teller (BET) specific surface area, pore volume, and pore diameter were calculated using multi-point N_2 adsorption/desorption isotherms. The pore size distribution was determined by the Barrett–Joyner–Halenda (BJH) method using the desorption branch of the N_2 isotherms. XRD patterns were recorded with an X-ray diffractometer (Bruker Co., Ltd, D8 Advance, Germany) equipped with Ni-filtrated Cu Kα1 radiation (λ = 0.15406 nm) and operating at 40 kV and 40 mA. The sorbent crystalline size and lattice constant were obtained from Debye–Scherrer and Bragg formula, respectively. The micro structures of the fresh, used and regenerated sorbents were investigated by a FEI XL-30 FEG field-emission scanning microscope (Phillips, Co., Ltd, Netherlands) operated at 5 kV. The chemical analysis was taken on the New XL-30 energy-dispersive X-ray spectroscopy (EDX) from EDAX Co., Ltd, USA. Fourier transform infrared spectroscopy (FTIR) absorption spectroscopy was performed with a FTIR-8400S spectrometer (Shimadzu Corporation, Japan) at room temperature with sample embedded in a KBr wafer. The temperature programmed reduction (H_2-TPR) analysis was performed on the ChemiSorb 2720 chemisorption analyzer from Micromeritics Instrument S&T Co., Ltd, USA. About 50 mg of sorbent was charged into a U-shape quartz reactor and pre-treated in Ar with a flow rate of 30 mL/min at 100 °C for 30 min followed by natural cooling to room temperature. Then the sorbent was heated from room temperature to 800 °C in a 10%H_2/Ar mixture with a flow rate of 40 mL/min at a rate of 10 °C/min. X-ray photoelectron energy spectroscopy (XPS) analysis was carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Kα radiation ($h\nu$ = 1253.6 eV) or Al Kα radiation ($h\nu$ = 1486.6 eV). To compensate for surface charge effects, the binding energies were calibrated using the C1s hydrocarbon peak at 284.6 eV.

2.2. Desulphurization/regeneration performance

Sulfidation tests were performed at atmospheric pressure in a vertical fixed bed quartz-tube microreactor (10 mm inner diameter, loaded with 0.2 g of sorbent) to evaluate the desulphurization performances of xCeyMn/ZSM-5 at 50 mg/m^3 H_2S breakthrough [20]. The quartz-tube microreactor was placed in a temperature controlled tubular furnace to control the reaction temperature and a thermocouple placed in the center of the sorbent bed was used to measure the reaction temperature. The flow rate of the feeding gas with weight hourly space velocity of 45,000 mL h^{-1} g^{-1} was precisely controlled by mass flow controller. The samples were first heated to the desired reaction temperature at a N_2 atmosphere to remove the impurities adsorbed on the sorbent surface. After sulfidation, pure N_2 was introduced to purge the desulphurization system until the sorbent bed was cooled to ambient temperature [26]. The H_2S concentration of the outlet gas was continuously measured by a gas chromatography (Fuli Analytical Instrument Co., Ltd, GC9790IIH-2, China) equipped with a flame photometry detector (FPD) for low concentrations of sulfur compounds and thermal conductivity detector (TCD) for high concentrations of sulfur compounds.

The breakthrough time was defined as the duration before the breakthrough point, and the sulfur capacity (SC) was obtained by the formulas

$$SC\left(\frac{\mu mol \ of \ sulfur}{g \ of \ sorbent}\right) = \frac{WHSV}{V_m} \times \left[\int_0^t (C_{in} - C_{out}) dt\right] \quad (1)$$