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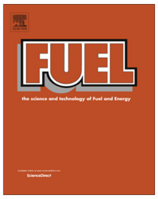

# $La_2CuO_4$/ZSM-5 sorbents for high-temperature desulphurization

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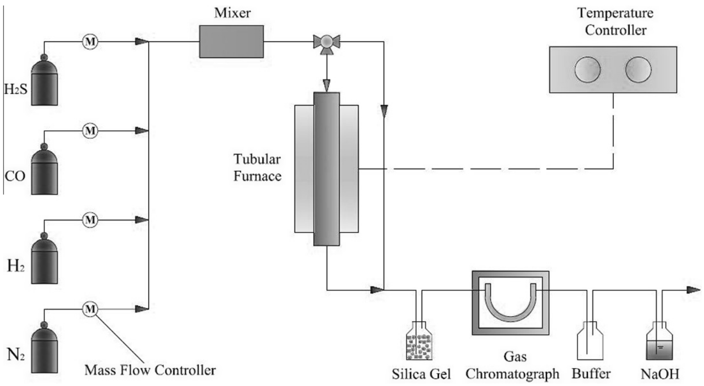
## HIGHLIGHTS

- The sulfidation activity of $La_2O_3$ was remarkably enhanced by introduction of Cu.
- 5La5Cu/ZSM-5 sorbent had the highest sulfur capacity of 2240.5 μmol S/g.
- $H_2$ suppressed sulfur removal but CO had a little influence on sulfidation reaction.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The high-temperature $H_2S$ removal was conducted over *x*La*y*Cu/ZSM-5 sorbents prepared via citric acid method. The sorbents showed good desulphurization performance, the maximal sulfur capacity of 2240.5 μmol S/g over 5La5Cu/ZSM-5 was achieved at 700 °C. The presence of $H_2$ obviously shortened the breakthrough time and reduced the sulfur capacity. However, the presence of CO had little influence on the desulphurization behavior. The sulfidation activity of $La_2O_3$ can be significantly enhanced by introduction of Cu due to the intimate mixing of $La_2O_3$ and CuO, the formation of $La_2CuO_4$ compound.

## 1. Introduction

Hydrogen sulfide ($H_2S$) is the main sulfur compounds in biogas, fuel cells and coal gasification plants; it is also a major air pollutant when it is emitted to atmosphere [1–3]. In addition, $H_2S$ can cause severe corrosion of downstream equipment, therefore has to be removed before syngas utilization. The temperature of the syngas form coal gasification usually exceeds 500 °C, traditional sulfur-removal method, such as ammonia absorption, can operate at a much lower temperature than syngas temperature [4], thus, hot coal gas has to be cooled down to ambient temperature and then preheated to high temperature again before feeding into gas turbine, which would reduce the thermal efficiency and greatly increase the system economic cost [5].

To lower the economic cost and improve the thermal efficiency, transition metal oxides [6], such as ferric oxide [7,8], copper oxide [9,10], and manganese oxide [11,12], zinc oxide [13,14], which can

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adsorb $H_2S$ at a higher temperature, would be a better choice for syngas purification. Binary and ternary oxides had also been extensively investigated for sulfur removal at moderate and high temperature, such as Fe–Mn [15], Mn–Cu [16], Zn–Mn [17] based sorbents, and zinc ferrite [18,19], zinc titanate [20]. Recently, Lanthanide oxides containing transition metal ions have attracted considerable interest because of their high reaction activity and good thermal stability in the field of VOCs [21] and methane [22] catalytic combustion, CO catalytic oxidation [23], NO decomposition [24], $H_2$ production [25], they had also been used for sulfur removal at high temperature because of their good thermal stability and high degree of purification [26,27]. However, the main defect of single-metal oxide or composite oxide is the low surface area and easy to be sintering during the high-temperature preparation and sulfidation process [28]. Dispersion of single-metal oxide or composite oxide on suitable refractory supports would increase the sorbent activity and thermal resistance. As we know, $\gamma$-$Al_2O_3$ was one of the most commonly used supports, however, the activity often reduced as a result of the interactions between active phase and the support, resulting in the formation of mixed oxides or the inclusion of transition metal ions into alumina lattice [29]. Zeolite (ZSM-5) of tunable structure, acid density, and shape selectivity can sustain long treatment under steam above 500 °C [30,31], it has been extensively used as a support or a catalyst in the field of selective catalytic reduction (SCR) [32], NO adsorption [33], NO decomposition [34], and petrochemical industry [35].

$La_2CuO_4$ was supported onto ZSM-5 and employed for sulfur removal at temperature ranging from 550 °C to 750 °C. The $H_2S$ adsorption mechanism over $La_2CuO_4$/ZSM-5 were investigated via means of studying the effects of sorbent microstructure, crystalline size, surface area, pore volume, and state of active species on the desulphurization performance. The sulfidation experiments were then performed to evaluate the impacts of reaction temperature, sorbent composition, $H_2$ content, and CO content on the sulfidation activity.

## 2. Experimental

### 2.1. Sorbent preparation and characterization

*x*La*y*Cu/ZSM-5 sorbents with a specific Cu mole fraction of 10%, 30%, 50%, 70%, and 90% prepared by sol–gel method were denoted as 9La1Cu/ZSM-5, 7La3Cu/ZSM-5, 5La5Cu/ZSM-5, 3La7Cu/ZSM-5, and 1La9Cu/ZSM-5, respectively. Stoichiometric amounts of lanthanum nitrate $La(NO_3)_3 \cdot 6H_2O$ (AR, Aladdin Reagent, Inc., China) and copper nitrate $Cu(NO_3)_2 \cdot 2.5H_2O$ (AR, Aladdin Reagent, Inc., China) were dissolved in 25 mL of nitric acid (~2 mol/L). After addition of citric acid with a mole amount of 1.5 times that of the total metal ions, ZSM-5 (Catalyst Plant of Nankai University, the mass fraction of ZSM-5 to the sorbent was 50%) was added to the aforementioned solution. The mixture was kept at 60 °C over a water bath until a viscous gel was formed. 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 in a muffle furnace. Eventually, all sorbents were pressed, ground and sieved (80–100 meshes) [36]. Additionally, ZSM-5 went through the same functionalization pathway without the use of the La and Cu precursors, the ZSM-5 sample after above processing was denoted as treated ZSM-5.

$N_2$ adsorption/desorption isotherms were measured at 77 K in a Beishide 3H-2000PS4 apparatus (Beishide Instrument S&T Co., Ltd, China). Prior to analysis, samples were 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 obtained by the Barrett–Joyner–Halenda (BJH) method. XRD patterns were recorded with an X-ray diffractometer (Bruker Co., Ltd, D8 Advance, Germany) equipped with Ni-filtrated Cu K$\alpha$1 radiation ($\lambda$ = 0.15406 nm) and operating at 40 kV and 40 mA. The sorbent crystalline sizes and lattice constants were calculated from Debye–Scherrer and Bragg formula, respectively. The micro structures of the fresh and used 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 performed on a 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, the sorbent was then heated from room temperature to 750 °C at a rate of 10 °C/min in a 10% $H_2$/Ar mixture with a flow rate of 40 mL/min. X-ray photoelectron energy spectroscopy (XPS) analysis was carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg K$\alpha$ radiation ($h\nu$ = 1253.6 eV) or Al K$\alpha$ radiation ($h\nu$ = 1486.6 eV). To compensate for surface charge effects, the binding energies were calibrated using the C1 s hydrocarbon peak at 284.6 eV.

### 2.2. Sorbent desulphurization and regeneration

Desulphurization performance at 50 mg/m$^3$ $H_2S$ breakthrough was evaluated at atmospheric pressure in a vertical fixed bed reactor (10 mm inner diameter, loaded with 0.2 g sorbents) [37]. A thermocouple placed in the center of sorbent bed was used to measure the reaction temperature. The flow rate of the feeding gas was precisely controlled by a mass flow controller. The sample was first heated to the desired reaction temperature in a $N_2$ atmosphere to remove impurities adsorbed on the sorbent surface. After sulfidation, pure $N_2$ purged the system until the sorbent bed was cooled to ambient temperature. The $H_2S$ concentration of the outlet gas was continuously measured by a gas chromatograph (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; the sulfur capacity was obtained by the formulas

$$S_{cap} = \frac{W_m}{V_m} \times \left[ \int_0^t (C_{in} - C_{out}) dt \right] \quad (1)$$

where $S_{cap}$ indicates the breakthrough sulfur capacity of the sorbents (μmol S/g), $W_m$ is the weight hourly space velocity (L h$^{-1}$ g$^{-1}$), $V_m$ means molar volume of $H_2S$ at 1 atm and 25 °C (24.5 L/mol), $t$ stands for the breakthrough time (h), $C_{in}$ and $C_{out}$ denote the inlet and outlet $H_2S$ concentration (ppmv), respectively. The sorbent was regenerated at 700 °C in a 5.0% $O_2/N_2$ mixture with $W_m$ of 30,000 mL h$^{-1}$ g$^{-1}$ on a fixed bed until no sulfur element formation and the characteristic peak of $SO_2$ in the effluent was no longer detected by the gas chromatograph. Eventually, 5.0% $O_2/N_2$ mixed gas was switched into $N_2$ and the sorbent was treated in pure $N_2$ at 700 °C for 1 h to decompose the sulfate formed at the regeneration process.