



# Low temperature desulfurization on Co-doped $\alpha$ -FeOOH: Tailoring the phase composition and creating the defects

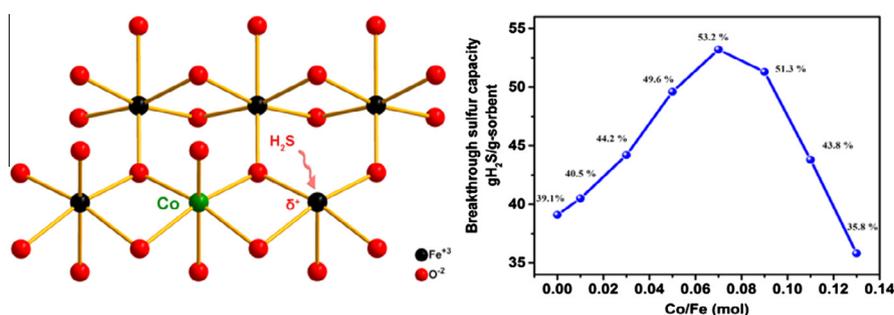
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## HIGHLIGHTS

- Co-doped  $\alpha$ -FeOOH was prepared via a simple co-precipitation method.
- By varying molar ratios of Co:Fe, the composition can be freely manipulated.
- The obtained samples show strikingly high sulfur capacity at room temperature.
- The increased surface area and defects contribute to the improved activity.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this paper, a series of Co-doped  $\alpha$ -FeOOH (Goethite) is prepared via a simple co-precipitation method. The obtained samples are characterized in detail by the powder X-ray diffraction (XRD), N<sub>2</sub> adsorption-desorption isotherms, X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), Raman spectroscopy and electron spin resonance (ESR). H<sub>2</sub>S adsorption experiments indicate that the Co-doped  $\alpha$ -FeOOH samples show strikingly high breakthrough sulfur capacity at low temperature (25 °C). The maximum count reaches 53.2% at Co/Fe = 0.07, which is much higher compared to that of the undoped  $\alpha$ -FeOOH sample. The improved activity could be mainly attributed to the larger surface area of  $\alpha$ -FeOOH and the increased lattice defects like oxygen vacancy arising from the incorporation of Co<sup>2+</sup> into  $\alpha$ -FeOOH structure.

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## 1. Introduction

With the development of human society, a large amount of hydrogen sulfide (H<sub>2</sub>S) is released from coal gasification, natural gas refineries and the metal smelting process of the steel industry, etc. This toxic gas is not only harmful to the environment, but also poisonous to the catalysts and corrosive to the metals pipeline [1–5]. Therefore, the removal of H<sub>2</sub>S is of great importance from the point of industrial catalytic processes and environment protection. Among various techniques developed for H<sub>2</sub>S removal, H<sub>2</sub>S

adsorption by the sorbent is considered to be the most applicable processes due to the high efficiency, reliability, and availability of a wide range of sorbents and working temperatures [6,7].

Over the past few years, various materials have been investigated for H<sub>2</sub>S adsorption [8–11]. Intensively, Zinc oxide and zinc-based materials have been studied as desulfurization sorbents due to their favorable sulfidation thermodynamics and high sulfur capacity [12–14]. However, high temperature (~300 °C) is required for efficient desulfurization over zinc-based materials. The development of the sorbents that can find applications in low-temperature desulfurization is needed. Recent studies indicate that sorbents based on transition metal oxides such as oxides of Co, Cu, Mn, Cr, Fe, Ni, and W are possible candidates for low temperature

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desulfurization [15–17]. However, the reported materials still suffer from the limitations for lowering of the desulfurization operating temperatures while maintaining satisfactory sulfur sorption capacities. In our earlier work, we demonstrated that  $\alpha$ -FeOOH showed considerable breakthrough sulfur capacity at room temperature for H<sub>2</sub>S removal [18]. Moreover, iron is low-cost and can be easily regenerated, showing great promise in low temperature desulfurization. Despite the progress, their sulfur capacity and desulfurization precision are not comparable to those of the zinc-based materials at high temperature and still need further improvement.

Enormous efforts have been focused on improving the H<sub>2</sub>S adsorption performance of metal oxides. Metal doping in metal oxides has been considered to be a promising way [19]. Metal dopants could modify the affinity of sorbent to bind H<sub>2</sub>S, leading to the improved capacity for H<sub>2</sub>S adsorption. Moreover, metal doping would introduce the defects on metal oxides, which in turn plays a significant role in the performance [20]. Previous study has shown that the addition of low valence metals such as La<sup>3+</sup> to CeO<sub>2</sub> would generate extrinsic oxygen vacancies [21]. And these oxygen vacancies may serve as active sites for surface adsorption and dissociation of H<sub>2</sub>S, and may also increase bulk diffusion rates of sulfur atoms within the ceria lattice to facilitate bulk sulfidation [22]. Thus, we can envision that the metal doping of  $\alpha$ -FeOOH may lead to the enhancement of the H<sub>2</sub>S adsorption performance. Recently, some metal-doped FeOOH have been synthesized and used as supports for gold [23] or as catalysts for chemical processes like Fenton reaction [24–26]. However, the reports on metal doped  $\alpha$ -FeOOH for H<sub>2</sub>S removal are rather scarce.

Herein, Co-doped  $\alpha$ -FeOOH sorbents are prepared by a facile coprecipitation method using sodium carbonate as the precipitant. Cobalt is chosen as a dopant because of the similar ionic radius between Co<sup>2+</sup> and Fe<sup>3+</sup>. Moreover, the low valence Co<sup>2+</sup> would help to create the lattice defects when it substitutes the higher valence Fe<sup>3+</sup>. The physicochemical properties of samples are characterized by various techniques. Their activities for H<sub>2</sub>S adsorption are evaluated at room temperature. Furthermore, the effects of Co doping on the H<sub>2</sub>S adsorption performances are investigated in detail. It is hoped that the present study might provide a feasible method to fabricate materials with high H<sub>2</sub>S adsorption performances at low temperature.

## 2. Materials and methods

### 2.1. Preparation of Co-doped $\alpha$ -FeOOH samples

FeSO<sub>4</sub>·7H<sub>2</sub>O (AR), CoSO<sub>4</sub>·7H<sub>2</sub>O (AR) and Na<sub>2</sub>CO<sub>3</sub> (AR) were purchased from Sinopharm Chemical Reagent Co. Ltd. All materials were used as received without further purification. Co-doped  $\alpha$ -FeOOH samples were prepared by coprecipitation method with Co (II) at a series of atomic ratios (Co/Fe) in the range 0–0.13. FeSO<sub>4</sub>·7H<sub>2</sub>O aqueous solution (1.0 M) was pre-made and filled in the reactor. A determined quantity of CoSO<sub>4</sub> was added to the above solution and stirred at 600 rpm using a mechanical stirrer (IKA RW20 digital) under the condition of air isolation. The mixed solution pH was adjusted to 9 with an aqueous solution of Na<sub>2</sub>CO<sub>3</sub> (2.4 M) at a constant rate. After precipitation, the suspension was exposed to air and crystallized at 40 °C for 3 h under continuous stirring, during which the pH was kept constant. The resulting precipitate was then washed with de-ionized water to remove sulfate ions and sodium ions, followed by centrifugation and drying at 80 °C for 16 h. By varying atomic ratios (Co/Fe) from 0 to 0.13, a series of samples were prepared and denoted as FeCo-*x*, where *x* refers to 0.01, 0.03, 0.05, 0.07, 0.09, 0.11, 0.13, respectively.

### 2.2. Characterization of the samples

The Powder X-ray diffraction (XRD) patterns of the sorbents were recorded in the 2 $\theta$  range of 10–90° on a PANalytical diffractometer (X'PertPro, Panalytical Corp.) with an X'Celerator detector, employing Co K $\alpha$  radiation source ( $\lambda$  = 0.179 nm) generated at 40 kV and 40 mA. BET surface area and the N<sub>2</sub> adsorption were carried out on an ASAP2020 M apparatus (Micromeritics Instrument Corp.). Chemical composition and the states of the elements in the samples were investigated by the X-ray Photoelectron Spectroscopy (XPS) on a Thermo Scientific ESCALAB 250 spectrometer. XPS data were calibrated using the binding energy of C1s (284.6 eV) as the standard. The contents of Co and Fe in the sorbents were determined through the Optima Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, OPTIMA 8000, Perkin Elmer Corp.). The Raman measurements were conducted on a multichannel modular triple Raman system (inVia Reflex, Renishaw Corp.) with confocal microscopy at room temperature excited with the 532 nm line of an Ar laser. The Scanning electron microscopy (SEM) images were obtained on a scanning electric microscope (XL30-ESEM, Philips Corp.). The electron spin resonance (ESR) characterization of the defects of the sorbents was carried out on A300 spectrometer (Bruker Corp.) at room temperature.

### 2.3. H<sub>2</sub>S breakthrough capacity test

H<sub>2</sub>S breakthrough capacities of the samples were measured at 25 °C using a fixed bed. 0.5 g of sample was loaded in a quartz tube (internal diameter 5 mm). A 4% H<sub>2</sub>S/N<sub>2</sub> gas stream was passed through the fixed bed of the sorbent particles at a WHSV of 2400 mL·h<sup>-1</sup>·g<sup>-1</sup>. The stream volume was recorded by a wet gas flow meter equipped just after the reactor exit. The exhaust gas needs to be continuously passed through a 0.1 M aq. solution of AgNO<sub>3</sub> as an indicator. The breakthrough time was measured as the time from the beginning of desulfurization process to the time when the indicator solution turns from colorless to black. Then the H<sub>2</sub>S concentration was further monitored by gas chromatography (FULI, 9790II) equipped with a flame photometric detector (FPD). At this time, the breakthrough concentration of H<sub>2</sub>S reached 1 ppm and the test was stopped. The breakthrough sulfur capacity expressed in grams of H<sub>2</sub>S per gram of the sample was calculated by the equation:

$$X = \frac{V \times C \times 32}{(22.4 \times G)(1 - C)} \times 100$$

where X is the sulfur capacity (%), V is the stream volume (L), C is the H<sub>2</sub>S concentration in the feed gas (%), G is the weight of adsorbent (g), 22.4 is the molar volume of gas at standard state (L/mol), 32 is the molar weight of S (g/mol).

## 3. Results and discussion

### 3.1. Structural studies

Fig. 1 shows the XRD patterns of the as-synthesized  $\alpha$ -FeOOH and the FeCo-*x* samples. For the  $\alpha$ -FeOOH (without Co), all the diffraction peaks can be well matched with the standard pattern of  $\alpha$ -FeOOH (PDF no. 00-029-0713). No impurity peaks are detected from the XRD. The FeCo-*x* with low Co doping concentration (Co/Fe < 0.07) exhibits similar XRD patterns to that of the pure  $\alpha$ -FeOOH. No obvious shifts in the 2 $\theta$  values are observed for the diffraction peaks, indicating that doping with a certain amount of Co could not induce a change of the crystal orientation in the structure and the lattice spacing. This may be due to that the ionic radius of Co<sup>2+</sup> (0.74 Å) is close to that of Fe<sup>3+</sup> (0.65 Å). With further

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