



Innovative low temperature regenerable zinc based mixed oxide sorbents for synthesis gas desulfurization



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HIGHLIGHTS

- ZnO and MoO₃ based materials have been studied as regenerable sulfur sorbents.
- Composite oxides show regeneration temperature up to 300 °C lower than ZnO sorbents.
- Transitional phases formations were evidenced through *in situ* XRD.
- Regeneration of sulfided mixed oxide is shown to exhibit synergetic effects.
- Synergetic effects result from exothermic oxidative reactions of molybdenum phases.

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ABSTRACT

Zinc oxide-based materials are commonly used for the final desulfurization of synthesis gas in IGCC and Fischer–Tropsch based XTL processes. The formation of large amount of solid waste is the major issue of this process. *In-situ* oxidative regeneration is a promising way to reduce this waste formation and enhance desulfurization process efficiency and economics. However, previous studies showed that one of the major drawbacks of oxidative regeneration of sulfided oxides relies in the high operating temperature range required to overcome the formation of inhibitory sulfate phases. A preliminary work of the authors focused on single oxides identified that regeneration temperature of zinc oxide-based sorbent could be reduced through the addition of molybdenum oxide. Two composite oxides – a single oxides mixture (ZnO and MoO₃) and a mixed oxide (ZnMoO₄) – were synthesized and characterized. Their sulfidation and oxidative regeneration properties were investigated through thermogravimetry and *in-situ* characterizations. Sulfidation of the single oxides mixture was shown to be similar to the combination of the sulfidation of both independent single oxides. Mixed oxide sulfidation leads to ZnMoO₄ phase demixing into ZnS, MoS₂ and ZnMoO₃. The oxidative regenerations of the sulfided single oxide mixtures and mixed oxide are initiated, respectively, at 350 °C and 300 °C. These temperatures are 250 °C and 300 °C lower than the regeneration temperature of a pure ZnS. For the sulfided mixed oxide regeneration is even complete at 500 °C under isothermal conditions. Regeneration of sulfided oxides mixture and mixed oxide was thus shown to exhibit synergetic effects, resulting from exothermic oxidative reactions of molybdenum phases. Heat energy released during these reactions is assumed to enhance ZnS oxidation kinetics at a temperature lower than the previously measured one.

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1. Introduction

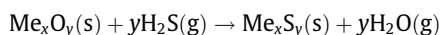
Integrated Gasification Combined Cycles (IGCC) power generation processes and Fischer–Tropsch based XTL processes (XTL for X = Biomass, Coal, or Gas To Liquids) constitute efficient and

cleaner alternative technologies for future energy production [1–3]. Both technologies are based on a first step of feed gasification into a synthesis gas or syngas, composed mainly of a mixture of CO and H₂ [4]. In IGCC processes, the syngas is burnt into a gas turbine to produce electrical energy. In the XTL processes, the syngas is converted into hydrocarbon fuel *via* the Fischer–Tropsch reaction [5–7]. Hydrogen sulfide constitutes one of the main impurities of synthesis gases [8]. This compound mixed to H₂, is responsible

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for the corrosion of the industrial units [9], especially the combustion turbine blades used in the IGCC. On another hand, it is also a poison of Fischer–Tropsch catalysts (cobalt-, iron-, and ruthenium-based) because of its irreversible chemisorption on their active sites [10–12]. Therefore, the sulfur content specifications in syngas are very drastic for such industrial units, below 10 ppmv for IGCC [13,14] and 0.05 ppmv for XTL [15,16]. Syngas bulk desulfurization is commonly conducted by chemical or physical solvents [17,18], though these technologies do not allow to achieve complete H₂S removal. Indeed, expected H₂S syngas content at solvent-based acid gas removal systems outlet (in the range 0.1–1 mol. ppm) remains higher than sulfur syngas content tolerated at Fischer–Tropsch process inlet [8,11]. Therefore deep desulfurization of syngas is generally achieved with solid sorbents based on metal oxides which can irreversibly react with H₂S according to the following generic reaction:



Because of the important and various initial amounts of H₂S (1–10,000 ppm) [19], the drastic sulfur specifications required, and the large syngas flow rates to be treated (around 100 kg s⁻¹ for an IGCC power plant) [20], the use of metal oxides based sorbents imposes either huge amounts of solids with large reactor or the use of small reactors and frequent changes of solid sorbent. In both cases, the large amount of solid waste produced is the major disadvantage of the sorbent-based syngas desulfurization, and may also alter process operation, efficiency, and economics. The *in-situ* regeneration of the sulfided sorbent, back to the oxide phase, during the process is an identified solution to improve desulfurization processes.

The optimization of such regenerable H₂S sorbent should be guided by two main targets: (1) offering irreversible sulfidation reaction when in contact with H₂S in order to minimize to the lowest possible level the H₂S concentration in the syngas, and (2) being able to get back to the oxide state when in contact with O₂ at the lowest possible temperature. The sulfidation and oxidative regeneration properties of single oxides were studied in the literature through thermochemical calculations [21–24]. It could be concluded from these studies that the single oxide sulfidation reaction was strongly affected by the syngas reductive atmosphere. Under these conditions, ZnO can be reduced into Zn which volatilized above 600 °C [25], reductions of CuO [26], Fe_xO_y [27] and Mn_xO_y [28] are faster than the related sulfidation reactions. Moreover, the sulfidation of Cu or Fe and the reduced manganese oxide are kinetically limited [26,27,29]. The sulfidation equilibrium of CeO₂ in reductive atmosphere seems to be favorable and leads to the formation of Ce₂O₂S [30].

However, the formation and thermal stability of refractory sulfate phases in oxidative regeneration conditions were pointed out as the main issues of this regeneration process [24,31–33]. Indeed sulfate formation leads to a decrease of the sorbent reactivity and durability [29,34,35], and detrimental particles sintering is favored at the high regeneration temperature required for sulfate decomposition [36]. Furthermore, the high temperatures required for the sulfate decomposition will affect the overall thermal efficiency of the process and will impose the use of refractory alloys to manufacture the industrial reactors [20].

In order to overcome the limitations of single oxide-based sorbents, “composite oxide sorbents” such as for example zinc ferrite (ZnFe₂O₄) [37], zinc titanate (Zn_xTi_yO_{x+2y}) [38], or copper chromite (CuO–CrO₂) [39] were developed through a series of incremental improvements in order to stabilize the long-term performance of H₂S sorbent [40], optimize the operating conditions of the process [41], and decrease the regeneration temperature below 500 °C [41–44].

In a previous work [45], a global approach was proposed to study the physical and chemical phenomena involved during both sulfidation and regeneration steps of single oxides and corresponding sulfides by a confrontation between thermochemical calculations and experimental approaches. Some single oxides were thus identified to design a low temperature regenerable H₂S sorbent. In particular, zinc oxide was shown to exhibit high sulfidation ability and restricted sulfate formation upon the ZnS surface particles during the oxidative regeneration process, in comparison to other sulfides of transition metal such as copper, manganese or iron. MoO₃ shown attractive properties, as the oxidative regeneration of the sulfided MoO₃ occurs through fast, highly exothermic and complete reaction below 500 °C.

Regarding the distinct properties of these two metal oxides, we focus in this paper on the reactivity of two different zinc and molybdenum based materials: a ZnO and MoO₃ single oxides physical mixture and the ZnMoO₄ mixed oxide. The objectives of this work are to evaluate the difference between the two materials and to identify potential synergetic effects between zinc and molybdenum phases, to study the physical and chemical phenomenon involved in sulfidation and oxidative regeneration reactions of these materials, and to validate the global approach previously proposed.

2. Materials and methods

2.1. Oxide materials syntheses

The single oxides mixture, ZnO–MoO₃ was obtained by physical milling of MoO₃ and ZnO materials. ZnO material was synthesized from thermal decomposition of precursor at 500 °C for 2 h. The precursor was (ZnCO₃)₂·(Zn(OH)₂)₃ (Aldrich, purity > 58% Zn). MoO₃ precursor was obtained from a chemical supplier, and was used as received after material characterizations.

Mixed oxide ZnMoO₄ material was synthesized by successive calcinations steps at 450 °C and 500 °C and physical milling of the previous ZnO–MoO₃ single oxides mixture.

2.2. Thermogravimetry measurements

The sulfidation of the composite oxides was followed by thermogravimetric analysis (TGA) at 350 °C and atmospheric pressure, using a commercial magnetic suspension balance (Rubotherm). The feed was composed of 0.9% H₂S diluted in H₂ with a constant flow (10.8 NL h⁻¹). Oxide samples were firstly heated under a Helium flow up to 350 °C, and then the inlet valve was switched to the H₂S–H₂ mixture under isothermal conditions. Sulfidation step had been conducted for 12 h.

Oxidative regeneration reaction of the sulfided sorbents were followed by TGA–DSC (Netzsch STA-449C Jupiter). Experiments with linear temperature variation were conducted by heating sulfided samples in an oxidative gas mixture (5% O₂ in N₂) at 5 °C/min from 49 °C to 625 °C. Isothermal experiments were also conducted on sulfided samples, which were first heated at 5 °C/min to 500 °C under N₂, and then treated at 500 °C by an oxidative gas mixture (5% O₂ in N₂) for 2 h. This gas mixture composition was chosen to limit sulfate formation [45]. In both kinds of experiments, gas flow rate was set to 9 NL h⁻¹. The exhaust gases were analyzed by mass spectrometry (Netzsch QMS-430C Aeolos).

2.3. Materials characterizations

Materials crystalline phases were characterized by X-ray diffraction (XRD) using a PANalytical X'Pert PRO diffractometer operating with Cu Kα radiation (λ = 1.54182 Å). Materials textural

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