



Full Length Article

Thermodynamic aspects of gasification derived syngas desulfurization, removal of hydrogen halides and regeneration of spent sorbents based on $\text{La}_2\text{O}_3/\text{La}_2\text{O}_2\text{CO}_3$ and cerium oxides



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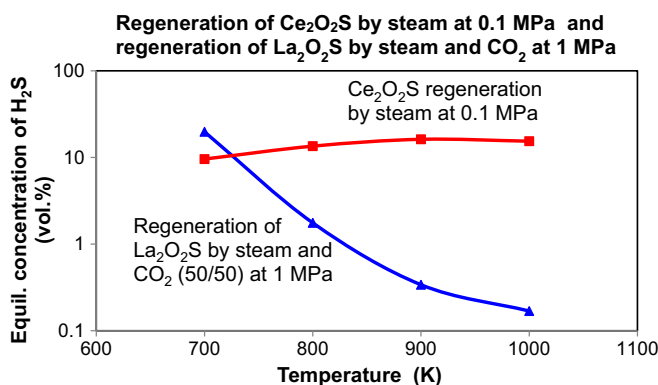
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HIGHLIGHTS

- Equilibrium concentrations of H_2S , COS, HCl and HF are computed for solid sorbents.
- The solid sorbents are based on pure solids: ZnO, cerium oxides, La_2O_3 and $\text{La}_2\text{O}_2\text{CO}_3$.
- Interferences of HCl and HF in de- H_2S reactions are determined ($T = 500\text{--}1100\text{ K}$).
- Minimization of Gibbs free energy for the complex systems is used.
- Possibilities of $\text{La}_2\text{O}_2\text{S}$ and $\text{Ce}_2\text{O}_2\text{S}$ regenerations are assessed.

GRAPHICAL ABSTRACT



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ABSTRACT

The thermodynamic analyses are focused on the determination of theoretical equilibrium concentrations of H_2S , HCl and HF for La_2O_3 , $\text{La}_2\text{O}_2\text{CO}_3$ and Ce_xO_y -based sulfur compounds sorbents, on possible interferences of hydrogen halides in H_2S removal in the temperature range 600–1100 K and on upstream selective deep removal of HCl and HF in producer gas. Minimization of Gibbs energy for the system was used in more complicated situations. The lowest H_2S concentration (<0.1 ppm-v) can be attained by Ce_2O_3 -based sorbents at temperatures below 800 K. Oxidation of the Ce_2O_3 -based sorbents to less efficient higher Ce-oxides (with limit of CeO_2) is thermodynamically preferred in real producer gas. Presence of CO_2 in gas phase leads to formation of lanthanum oxy-carbonate ($\text{La}_2\text{O}_2\text{CO}_3$) with lower efficiency in H_2S removal than La_2O_3 . The thermodynamic analyses are also focused on suitable ways and conditions for regeneration of spent desulfurization sorbents ($\text{Ce}_2\text{O}_2\text{S}$ and $\text{La}_2\text{O}_2\text{S}$) to the corresponding oxides or oxy-carbonates at temperatures 600 K–1100 K. The $\text{Ce}_2\text{O}_2\text{S}$ -based spent cerium sorbents are advantageously regenerated by reaction with SO_2 at temperatures over 700 K. In this way CeO_2 , elemental sulfur and small concentrations of S_2O are theoretically produced. If the cerium halides are formed, their decomposition and full Ce-sorbent regeneration is thermodynamically possible rather by reaction with steam. The La-based spent sulfur sorbents are restored by reaction with CO_2 and H_2O vapor leading to

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formation of $\text{La}_2\text{O}_2\text{CO}_3$ and H_2S . The suitable operating conditions involve temperatures between 700 and 800 K and higher operating pressures. Potential small contents of La-oxy-halides (LaOF and LaOCl) in the spent sorbent are converted into $\text{La}_2\text{O}_2\text{CO}_3$ in such a regeneration process.

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1. Introduction

Medium and high temperature (500–1200 K) desulfurization of producer gas from gasification of solid fuels (coal, coal-biomass blends, biomass, etc.) can be accomplished with Ca, Fe, Zn, Cu, Mn and rare earths oxides (REO) based sorbents [1–8]. For deep desulfurization of producer gas (e.g., for advanced applications of clean producer gas) mainly ZnO-based sorbents are still preferred. In the period of last 10 years, various solid sorbents based on CaO-BaO systems, cerium oxides and La_2O_3 have been suggested and studied for application in high temperature gas cleaning [6,8–11].

The raw producer gas from gasification of coal, biomass and their mixtures usually contains not only sulfur and tar related compounds (in the case of fluidized bed gasification), but also hydrogen halides (HCl and HF), which even in small concentrations can interfere with sulfur compounds sorption and lead to the formation of melted chlorides/fluorides (e.g., ZnCl_2) and eutectics at temperatures below 900 K. The content of HCl in fuel gas from gasification of wood [12] is approx. in the range 30–100 ppm-v, in gasification of herbaceous biomass, straw and coals [13,14] the content is higher, approx. between 200 and 700 ppm-v. Content of HF in raw fuel gas is usually 3–10 times lower [13] than the content of HCl and the data on HF content are relatively scarce. The HCl sorbents for medium/high temperature fuel gas and syngas dry cleaning are mentioned in literature [15–17]. The assessment of alkaline compounds based HF sorbents (thermodynamics and experimental sorption) for removal of higher concentrations of HF is mentioned in literature [15], but studies dealing with removal of lower concentrations of HF from gas by means of other sorbents (e.g., based on REE) at medium and higher temperatures and studies of interferences in gas desulfurization are missing in open literature.

The theoretical thermodynamic study of desulfurization and simultaneous interferences caused by the presence of HCl and HF in gas phase is complicated in the case of rare earth oxides (Ce_2O_3 , CeO_2 , La_2O_3 , Nd_2O_3 , etc.) by lack of reliable thermodynamic data (particularly ΔG_f) for some solid products [19–22] of desulfurization (oxy-sulfides) and dehalogenation (e.g., oxy-fluorides) [23].

The spent solid sorbents from producer or syngas medium/high temperature desulfurization (sulfidation) processes can be regenerated generally by three methods [21,24–28]: mild oxidation, reactions with steam (in fact the reverse sulfidation reaction) or by reactions with SO_2 leading to elemental sulfur production. The problems in application of the oxidation reactions for spent sorbents include highly exothermic reactions, necessity to use higher temperatures to overcome formation of stable sulfates (e.g., ZnSO_4), oxy-sulfates (e.g., $\text{La}_2\text{O}_2\text{SO}_4$) and highly thermodynamically stable basic sulfates (e.g., $\text{ZnO} \cdot 2\text{ZnSO}_4$) [29–32]. Necessity to use relatively high temperature and precisely defined oxygen/sorbent molar ratio is usually a practical obstacle for highly selective conversion to reactive (non-sintered) regenerated oxide. In regeneration by steam, the highest conversions to H_2S are attained for the less efficient H_2S sorbents [33] (e.g., CeO_2). More advantageous regeneration reactions with steam are those with the decreasing number of moles of gaseous products, because in such a case the higher operation pressure in H_2S desorption has a beneficial effect. But, the common steam regeneration reactions of

spent sulfide sorbent to metal oxides are equimolar in nature. Only the formation of e.g., stable carbonates/oxy-carbonates [34–36] instead of oxides leads to decreasing number of moles of gaseous compounds. Formation of elemental sulfur in the sorbent regeneration processes presents an advantage of versatile, easy-storable solid product. However, as indicated by thermodynamics [28,37], the only applicable regeneration reaction leading to elemental sulfur is reaction of $\text{Ce}_2\text{O}_2\text{S}$ with SO_2 . The oxidation regeneration reactions of $\text{Ce}_2\text{O}_2\text{S}$ are highly exothermic with excessive heat effects.

The $\text{La}_2\text{O}_3/\text{La}_2\text{O}_2\text{CO}_3$ based sorbents can be regenerated [38] after sulfidation by either oxidation or by reaction with H_2O vapor and CO_2 leading to lanthanum-oxy-carbonate ($\text{La}_2\text{O}_2\text{CO}_3$). The oxidation regeneration reactions, as the thermodynamics and TG analyses indicate [30,38], give rise to the formation of thermally very stable oxy-sulfate ($\text{La}_2\text{O}_2\text{SO}_4$) with the temperature of decomposition above approx. 900 °C (1200 K). The regeneration reaction with water vapor and CO_2 is enhanced by the increasing operating pressure. The formation of $\text{La}_2\text{O}_2\text{CO}_3$ is disadvantage from the point of view of efficient H_2S sorption, but on the other hand, significant content of CO_2 in producer gas (or syngas) causes transformation of La_2O_3 into $\text{La}_2\text{O}_2\text{CO}_3$ [27,28] at temperatures below approx. 800 °C.

Our thermodynamic analysis of gas desulfurization and hydrogen halides interferences is focused on the determination of theoretical equilibrium concentrations of HCl and HF for La_2O_3 , lanthanum carbonates/oxy-carbonates and Ce_xO_y -based sulfur compounds (H_2S , COS) sorbents and on the interferences of hydrogen halides on H_2S sorption (equilibrium concentrations) or possible reactions of relevant oxy-sulfides ($\text{La}_2\text{O}_2\text{S}$, $\text{Ce}_2\text{O}_2\text{S}$) with HCl and HF. The thermodynamic analyses involve systems with computations of gas composition on basis of assumption of solid phases with unit activity (stable, basic state). Effects of formation of mixed solid solutions on efficiency of removal of gas impurities are discussed and confronted with experimental data. In more complicated cases also the minimization of Gibbs energy for the model systems is used [39–41].

We have no ambition to suppose that design of gas–solid cleaning processes can be based only on theoretical thermodynamic analyses, but we suppose that the data are useful as some limits, applicable and valuable for praxis, where the equilibrium is not attained due to various reasons (insufficient time, diffusional limitations, changing activities of solid phases, etc.).

We considered here for thermodynamic analyses only reactions of Ce_2O_3 and CeO_2 , because thermodynamic data of the mixed stoichiometric Ce-oxides (Ce_xO_y) are often not available. Some of possible reactants ($\text{La}(\text{OH})_3$, CeOOH and LaOOH) have been not considered for analyses, because, under conditions of composition of wet fuel gas containing CO_2 and at higher temperatures (over 650 K), they are either decomposed or changed into more stable compounds (Ce_2O_3 , CeO_2 , La_2O_3 or $\text{La}_2\text{O}_2\text{CO}_3$) [42–45]. Moreover, the relevant thermodynamic data for LaOOH and CeOOH are unavailable for temperatures over 700 K.

Because in literature relatively often partly incomplete and partly controversial data can be found on the regeneration reactions, chemistry, thermodynamics, and kinetics, we analyze here possible chemical products and thermodynamics for several selected regenerations of $\text{Ce}_2\text{O}_2\text{S}$ and $\text{La}_2\text{O}_2\text{S}$, the realistic products of producer gas desulfurization. In the regeneration schemes also

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