Rational selection of single oxide sorbents for syngas desulfurization regenerable at reduced temperature: Thermochemical calculations and experimental study

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HIGHLIGHTS

- Oxides properties were studied in reductive sulfiding and oxidative conditions.
- Studied sulfided oxides require temperatures above 800 °C to complete regeneration.
- However, exothermic regeneration of MoO_2/MoS_2 mixture occurs form 400 °C.
- ZnO and MoO_3 based composites oxides may present promising properties.

ARTICLE INFO

ABSTRACT

Metal oxide based materials are commonly used for the final non-regenerative desulfurization of synthesis gas in IGCC and Fischer–Tropsch based XTL processes. *In situ* oxidative regeneration is a promising way to prevent massive waste formation resulting from usual H_2S scavenger processes, and leads to a global process efficiency and economics improvement. However, it is shown in the literature that refractory sulfate formation of sulfided oxides in oxidative conditions constitutes one of the major limitations for the development of an economic low temperature regeneration process. In the present paper, the authors propose a rational methodology to compare and identify single oxides most-suited for the regenerative desulfurization of syngas. This work brings novel insight through a systematic comparison of thermodynamic gas–solid equilibrium data and experimental study of sulfidation and oxidative regeneration of single oxides of interest. Based on equilibrium calculations, Ce, Cu, Fe, Mn, Mo and Zn oxides were selected for further experimental investigations, as they proved to offer the best compromise between the stabilities of their related sulfide and sulfate phases, respectively in reductive sulfiding and oxidative conditions. Sulfidation tests showed that Ce, Cu, Fe, Mn and Zn oxides were quantitatively transformed in their relative sulfide phases whereas Mo oxides could hardly be sulfided in the studied operating conditions. The oxidative regeneration of Ce, Cu, Fe and Mn-based sulfided materials led to a massive formation of sulfate phases which could only be decomposed at very high temperatures (>600 °C). At the opposite, zinc sulfatation was shown to be limited. The regeneration of MoO_2/MoS_2 mixture resulting from Mo oxide sulfidation was observed at reduced temperature (starting at 400 °C) without sulfate formation and proved to be very exothermic. All those results led the authors to state that no single oxide could offer optimal concomitant sulfidation and regeneration abilities required for an efficient regenerative syngas desulfurization process. However, this target could be achieved *via* a new composite materials that may combine several single oxides properties, exhibiting respectively high sulfur capacity, such as ZnO, and low regeneration temperature brought by the exothermic re-oxidation of sulfo-reduced MoO_3.

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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

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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 H_2 (+CO_2 and H_2O as main side-products) [4]. In IGCC the syngas is burnt into a gas turbine to produce electricity. In XTL processes, the syngas is converted into ultra-clean liquid hydrocarbon-based fuel *via* the Fischer–Tropsch reaction [5–7]. Hydrogen sulfide constitutes one of the main impurities of syngas. This compound, mixed to H_2, is responsible for the corrosion of the industrial units [8], such as the combustion turbine blades used in IGCC processes. On another hand, it is also a poison of Fischer–Tropsch catalysts (cobalt-, iron-, and ruthenium-based) because of its irreversible chemisorption on their actives sites [9–11]. Therefore, the sulfur content specifications in syngas are very drastic for such industrial units, below 10 ppmv for IGCC [12,13] and 0.05 ppmv for XTL [14–16]. The bulk desulfurization of the syngas is commonly performed by chemical or physical solvents [17,18]; though these technologies do not allow to achieve complete H_2S removal. Indeed, expected H_2S 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 [10,19]. Thus, the deep desulfurization of syngas is generally achieved with solid sorbents based on metal oxides, which irreversibly react with H_2S according to the following generic reaction:

$$Me_xO_y(s) + yH_2S(g) \rightarrow Me_xS_y(s) + yH_2O(g)$$
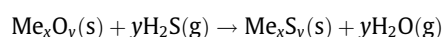
Because of the important and various initial amounts of H_2S (between 1 and 10,000 ppm) [20], the drastic sulfur specifications required, and the large gas flow rates of syngas to treat (around 100 kg/s for an IGCC power plant) [21], the use of metal oxides based sorbents imposes either huge amounts of solid with large reactor size or the use of small reactors and frequent changes of solid sorbent. In both cases, the large amount of solid wastes 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 regeneration process can be performed through three different routes [22]. The first one relies on oxidative regeneration: the sulfide is converted back to oxide *via* oxidation with air or diluted air. The second one is based on the reverse of the sulfidation reaction: the sulfide is reacted with H_2O (steam) to be converted into the oxide. The last one implies SO_2 as a regenerative gas: the oxide is obtained with a gaseous release of S_2. Although these processes present respective drawbacks, air-based oxidation appears as the simplest and most straightforward way in term of process operation for the *in situ* regeneration of sulfided oxide-based sorbents. Moreover, the oxidative regeneration was extensively studied in the field of metallurgy, and numerous related data are available in the literature [23–26].

Based on thermodynamic studies [27–30], the sulfidation properties of selected single oxides, as CaO, CeO_2, or ZnO, have been mainly investigated. The reactions occurring during these oxides sulfidation depend on the operating conditions, in particular the syngas reductive atmosphere. Indeed, CaO, CuO [31], Fe_xO_y [32] and Mn_xO_y [33] reactivity towards sulfidation is strongly affected by H_2, and ZnO can be reduced and volatilized above 600 °C [34].

Table 1
Solid phases selected for thermodynamic equilibrium calculations in sulfidation and oxidative regeneration conditions.

Initial oxides phase	Other selected phases for equilibrium calculations in sulfidation conditions	Initial sulfide phase	Additional selected phases for equilibrium calculations in oxidative regeneration conditions
Al_2O_3	Al_2S_3, Al	Calculations not performed	
BaO	BaS, Ba	BaS	BaO, $BaSO_4$, Ba
CaO	CaS, Ca	CaS	CaO, $CaSO_4$, Ca
CeO_2	$CeO_{1.72}$, $CeO_{1.81}$, $CeO_{1.83}$, CeS, CeS_2, Ce_2O_2S, Ce	Ce_2O_2S	CeO_2, $CeO_{1.72}$, $CeO_{1.81}$, $CeO_{1.83}$, CeS, CeS_2, $Ce(SO_4)_2$, $Ce2(SO_4)_3$, Ce
Co_3O_4	Co_9S_8, CoS_2, Co	Co_9S_8	Co_3O_4, CoS_2, $CoSO_4$, Co
CuO	Cu_2O, Cu_2S, CuS, Cu	Cu_2S	Cu_2O, Cu_2O, CuS, $CuSO_4$, Cu_2SO_4, CuO^*CuSO_4, Cu
Fe_2O_3	FeO, Fe_3O_4, FeS, Fe_2S, Fe_2S_3, FeS_2, Fe	FeS	Fe_2O_3, FeO, Fe_3O_4, Fe_2S, Fe_2S_3, FeS_2, $FeSO_4$, $Fe_2(SO_4)_3$, Fe
MgO	MgS, Mg	Calculations not performed	
Mn_2O_3	MnO, MnO_2, Mn_3O_4, MnS, MnS_2, Mn	MnS	Mn_2O_3, MnO, MnO_2, Mn_3O_4, MnS_2, $MnSO_4$, Mn
MoO_3	MoO_2, Mo_2S_3, MoS_2, Mo	MoS_2	MoO_3, MoO_2, Mo_2S_3, Mo
NiO	$NiS_{0.84}$, NiS, Ni_3S_4, NiS_2, Ni_3S_2, Ni	Ni_3S_2	NiO, $NiS_{0.84}$, NiS, Ni_3S_4, NiS_2, $NiSO_4$, Ni
SrO	SrS, Sr	SrS	SrO, $SrSO_4$, Sr
TiO_2	TiO, Ti_4O_7, TiS_2, TiS, Ti	Calculations not performed	
ZnO	ZnS, Zn	ZnS	ZnO, $ZnSO_4$, ZnO^*ZnSO_4, Zn
ZrO_2	ZrS_2, Zr	Calculations not performed	

Table 2
Input data of the equilibrium calculations.

			IGCC	XTL
Sulfidation	Simulated gas compositions (kmol)	N_2	55	55.32
		H_2	32.175	32.175
		H_2O	12.5	12.5
		H_2S	3250 ppm	50 ppm
	Operating conditions	P_{tot} (MPa)	3	
		T (°C)	150–450	
	Sorbents (kmol)	Me_xO_y	1	
Oxidative regeneration	Simulated gas compositions (kmol)	N_2	80/90/95	
		O_2	20/10/5	
	Operating conditions	P_{tot} (MPa)	3	
		T (°C)	150–450	
	Sorbents (kmol)	Me_xS_y	1	