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# Thermodynamic interferences of HCl and HF in producer gas desulfurization by Ce, La, Mn and Zn based solid sorbents

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## 1. Introduction

Producer gas from gasification processes of coals, biomass and waste fuels can be used for generation of electricity, production of hydrogen, synthetic transportation fuels and chemicals. The advanced applications of syngas (e.g. catalytic processes and fueling of high temperature fuel cells) require deep removal of contaminants (HCl, HF, H<sub>2</sub>S, COS organic sulfur compounds, tar compounds, volatile heavy metal compounds etc.) usually present in syngas. Their concentrations in syngas to be cleaned depends on fuel and conditions of gasification (moving/fixed bed, fluidized bed, entrained flow etc.). Among the gas contaminants, sulfur compounds, HCl and HF produced in the gasification process (e.g. fluidized bed process) belong to the most dangerous, which must be removed. Deep producer gas cleaning for attaining sulfur compounds and hydrogen-halides concentrations approx. below 1 ppm<sub>v</sub> (or even below 10 ppb<sub>v</sub>) requires either application of low temperature wet absorption processes or, particularly for fueling of high temperature fuel cells (SOFC), deployment of medium and high temperature (approx. 500 – 1200 K) cleaning methods based on reactions of gas impurities with solid sorbents. The important factors for hot syngas desulfurization and de-halogenation by solid sorbents are: attainable equilibrium concentrations at given gas composition and operating conditions (temperature, pressure), stability of the sorbents (sintering, melting, evaporation etc.), possible regeneration of a spent sorbent and price.

In literature mainly sorbents based on CaO, ZnO, Fe, Cu and Mn oxides are mentioned for removal of sulfur compounds (H<sub>2</sub>S, COS) [1-4]. Recently also sorbents based on rare earth oxides have been studied (both theoretically and experimentally) for deep syngas desulfurization [5-9]. Possibilities of removal of HCl from syngas by transition metals [1,9,10] and alkali based sorbents [1,11,12] at temperatures 200 – 800 °C have shown on possible applicability of soda and K<sub>2</sub>CO<sub>3</sub> based sorbents. Interferences of HCl and HF in H<sub>2</sub>S sorption by solid sorbents at higher temperatures have been studied only rarely [1,13]. Particularly studies (both, theoretical and experimental) of interferences in sulfur compounds sorption caused by HF and interferences of H<sub>2</sub>S in HF removal by alkali sorbents are missing in available literature.

The theoretical thermodynamic study of desulfurization and simultaneous interferences caused by presence of HCl and HF is complicated in the case of rare earth oxides ( $\text{Ce}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{La}_2\text{O}_3$ ,  $\text{Nd}_2\text{O}_3$ , etc.) by lack of reliable thermodynamic data (particularly  $\Delta G_f^\circ$ ) for solid products of desulfurization (oxy-sulfides), particularly for temperatures between 400 and 800 K [14,15]. Also the data for  $\text{Ce}_2\text{O}_2\text{S}$  and  $\text{La}_2\text{O}_2\text{S}$  at 298.15 K are scarce and partly disputable [15,16].

In our thermodynamic theoretical study we concentrated our attention on thermodynamics of gas-solid desulfurization reactions ( $\text{H}_2\text{S}$ , COS, thiophene), properties of sorbents (melting point evaporation), attainable equilibrium sulfur compounds concentrations in gas at temperature 500 – 1100 K (227-827 °C) under conditions typical for producer gas composition. Similarly removal of HCl and HF by Ce, La, Zn, Mn and Ni oxides based sorbents is described and possible interferences in simultaneous sorption of HCl or HF with  $\text{H}_2\text{S}$  are analyzed. Suitable conditions and sorbents are suggested for deep removal of sulfur compounds in presence of HCl. Conditions for efficient preliminary removal of HCl and HF by alkali-based sorbents ( $\text{NaHCO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{CaCO}_3$ ) are suggested and possible interferences caused by  $\text{H}_2\text{S}$  are analyzed in terms of attainable equilibrium concentrations of HCl and HF in presence of  $\text{H}_2\text{S}$ . Properties of La and Ce-based sorbents for sulfur compounds are compared with Zn, Mn and Ni based sorbents in terms of efficiency and interferences caused by presence of hydrogen-halides (HCl, HF).

## 2. Chemistry and Thermodynamics of Desulfurization and Removal of HCl (HF)

For theoretical studies of syngas desulfurization and interferences caused by HCl and HF in sulfur compounds sorption under reducing conditions we have chosen the main input oxides:  $\text{Ce}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{La}_2\text{O}_3$ , ZnO, MnO,  $\text{Cu}_2\text{O}$  and NiO. The considered products of desulfurization reactions under reducing conditions are cerium oxy-sulfide ( $\text{Ce}_2\text{O}_2\text{S}$ ), lanthanum oxy-sulfide ( $\text{La}_2\text{O}_2\text{S}$ ), zinc sulfide (ZnS), manganese sulfide (MnS), cuprous sulfide ( $\text{Cu}_2\text{S}$ ) and nickel sulfide (NiS) respectively. The two considered cerium oxides ( $\text{Ce}_2\text{O}_3$  and  $\text{CeO}_2$ ) are in fact limits in composition of Ce-oxide in real producer gas. As it was proved, the stoichiometry in cerium oxides varies approx. between  $\text{CeO}_{1.6}$  and  $\text{CeO}_{1.85}$  according to intensity of reduction conditions and temperature [6,8,17]. At temperatures over 800 K and under strongly reducing conditions the final composition of cerium oxide is close to  $\text{Ce}_2\text{O}_3$ . Formation of  $\text{Ce}_2\text{S}_3$  and  $\text{La}_2\text{S}_3$  is possible only under extreme conditions (high pressures of  $\text{H}_2\text{S}$ ,  $\text{S}_n$ ,  $\text{H}_2$ , CO and very low pressures of  $\text{H}_2\text{O}$  vapor and  $\text{CO}_2$ ). Under “usual” reduction conditions prevailing in syngas only the mentioned La and Ce oxy-sulfides are stable. Some transition and uncertainty in stoichiometry exists even in the case of  $\text{Ce}_2\text{O}_2\text{S}$ . It is interesting to note that existence of  $\text{Ce}_2\text{O}_{2.5}\text{S}$  has been clearly proved and properties of it were described [18].

Reactions of the above mentioned oxides with HCl lead to corresponding chlorides:  $\text{CeCl}_3$ ,  $\text{LaCl}_3$ ,  $\text{ZnCl}_2$ ,  $\text{MnCl}_2$ ,  $\text{CuCl}$  and  $\text{NiCl}_2$ . In the case of lanthanum, also oxy-chloride is stable and can be considered as one of the products ( $\text{LaOCl}$ ,  $\text{LaCl}_3$ ) of the reaction of  $\text{La}_2\text{O}_3$  with HCl. On the other hand,  $\text{CeOCl}$  is extremely unstable and is not considered here as possible product. In the case of reactions of HF with the mentioned oxides, generally only corresponding fluorides are formed. The values of Gibbs energy of formation ( $\Delta G_f^\circ$ ) of the compounds have been taken mostly from Barin tables [19]. The data for thiophene have been overtaken from J. Phys. Chem. Ref. Data [20]. The  $\Delta G_f^\circ$  data for  $\text{Ce}_2\text{O}_2\text{S}$  and  $\text{La}_2\text{O}_2\text{S}$  have been overtaken from other sources [6,14-16] and partly either interpolated or determined under assumption of linear dependence on temperature.

For reactions with HF and interferences in H<sub>2</sub>S sorption, fluorides ZnF<sub>2</sub>, MnF<sub>2</sub>, NiF<sub>2</sub> and CuF have been considered as products. The products of hydrogen fluoride (HF) reaction with La<sub>2</sub>O<sub>3</sub> and Ce<sub>2</sub>O<sub>3</sub> can be both, corresponding fluorides (LaF<sub>3</sub>, CeF<sub>3</sub>) or oxy-fluorides (LaOF, CeOF). The mentioned oxy-fluorides exist, have interesting physical (electric and optic) properties and both are relatively stable, but literature data on  $\Delta G_f$  and  $\Delta G_r$  for their reactions are available in literature [21] only for LaOF.

Removal of HCl and HF from syngas by gas-solid reactions [1,11,22] with Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, and calcium based sorbents (Ca-hydroxide and carbonate) have been considered.

The Gibbs energies  $\Delta G_r$  for individual reactions have been computed according to reaction stoichiometry and the general scheme:

$$\Delta G_r = \Sigma(\Delta G_f)_{\text{final compounds}} - \Sigma(\Delta G_f)_{\text{input compounds}} \quad (1.1)$$

The equilibrium reaction constant  $K_{eq}$  is thermodynamically related with  $\Delta G_r$ , absolute temperature  $T$  and the universal gas constant  $R$  through the following equation:

$$\ln(K_r) = [-\Delta G_r/(RT)] \quad \text{or} \quad K_r = \exp[-\Delta G_r/(RT)] \quad (1.2)$$

Computation of equilibrium pressures of gas or volatile species from the equilibrium constant is described elsewhere [23,24]. For simplicity unit activities of all solid reactants (compounds and elements) were considered in computations of equilibrium gas phase composition (partial pressures).

ZnCl<sub>2</sub>, MnCl<sub>2</sub>, CuCl and partially CaCl<sub>2</sub> are the main easy melting compounds (< 800 °C) among the reaction products (**Table I**). Moreover elemental Zn is relatively volatile.

**Table I:** Melting points (lower than 800 °C) and boiling points of selected compounds and metallic Zn relevant in removal reactions of H<sub>2</sub>S, HCl and HF from producer gas

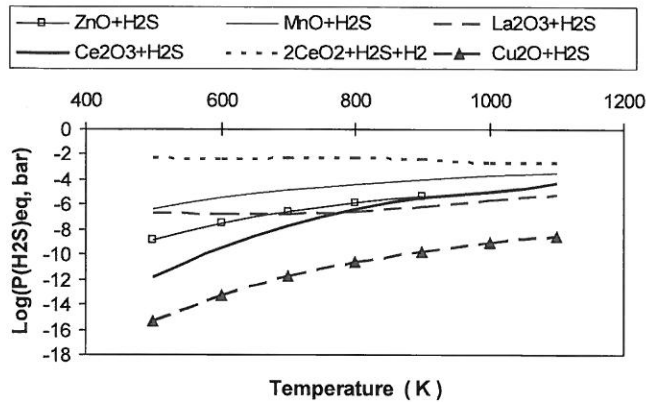
Compounds	Melting point (°C)	Boiling point (°C)	Notice
ZnCl <sub>2</sub>	292 (565 K)	756	Relatively volatile
Zn	419 (692.7 K)	907	Relatively volatile
CuCl	426 (771 K)	1490	
MnCl <sub>2</sub>	650 (923 K)	1225	
KCl	770 (1043 K)	1420	
CaCl <sub>2</sub>	772 (1045 K)		
NiS	797 (1070 K)	1388	

### 3. Results and discussion

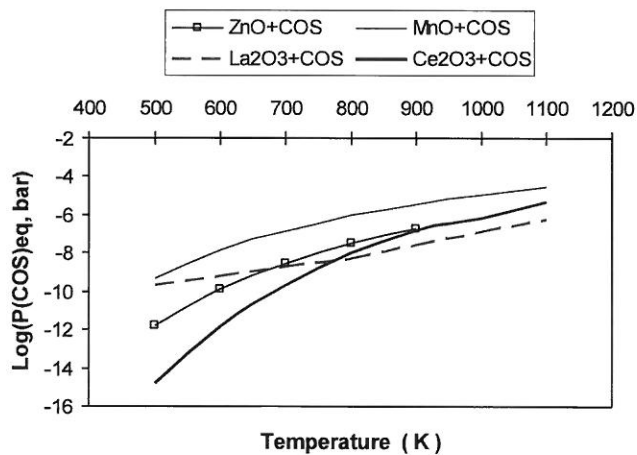
#### Desulfurization of syngas (Removal of H<sub>2</sub>S, COS and thiophene)

The equilibrium concentrations of H<sub>2</sub>S and COS in reactions with ZnO, MnO, Cu<sub>2</sub>O, Ce<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> at atmospheric pressure (1 bar) under assumption of 40 vol. % of hydrogen, 10 vol. % of water vapor and 30 vol. % of CO<sub>2</sub> in gas phase are shown in **Figs 1 and 2**. As it is obvious (**Fig. 1**), CeO<sub>2</sub> is not suitable for syngas desulfurization and must be reduced to Ce<sub>2</sub>O<sub>3</sub>

prior to reaction with H<sub>2</sub>S. At temperatures 600 – 800 K the ZnO, Cu<sub>2</sub>O, Ce<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub> based sorbents are able to ensure output concentrations of H<sub>2</sub>S and COS below 1 ppm<sub>v</sub> ( $P_{\text{H}_2\text{S}} < 10^{-6}$  bar) and below 10<sup>-2</sup> ppm<sub>v</sub> ( $P_{\text{COS}} < 10^{-8}$  bar) respectively. Cu<sub>2</sub>O exerts the lowest attainable H<sub>2</sub>S and COS equilibrium pressures (concentrations) in the frame of the sorbents studied ( $P_{\text{H}_2\text{S}} < 10^{-9}$  bar).



**Fig. 1:** Dependence of equilibrium H<sub>2</sub>S pressures (expressed as log( $P_{\text{H}_2\text{S}}$  - in bar) ) on temperature in reactions of H<sub>2</sub>S with the selected solid sorbents ( $P_{\text{H}_2} = 0.4$  bar,  $p_{\text{H}_2\text{O}} = 0.1$  bar)



**Fig. 2:** Dependence of equilibrium COS pressures (expressed in log( $P_{\text{COS}}$  - in bar)) on temperature in reactions of COS with the selected solid sorbents ( $P_{\text{CO}_2} = 0.3$  bar)

Attaining of equilibrium concentrations of H<sub>2</sub>S below 1 ppb<sub>v</sub> is theoretically possible only with Cu<sub>2</sub>O at temperatures below 1000 K or with Ce<sub>2</sub>O<sub>3</sub> based sorbents at lower temperature (< 600 K). The theoretically attainable equilibrium COS pressures are generally lower than the H<sub>2</sub>S equilibrium pressures. Very low equilibriums H<sub>2</sub>S pressures (corresponding concentrations below 1 ppb<sub>v</sub>) are exerted by the reaction of elemental Zn with H<sub>2</sub>S (**Table II**). The lowest equilibrium

H<sub>2</sub>S pressures are thus enabled by Cu<sub>2</sub>O or metallic zinc as solid input reagents. Stability of Zn and Cu<sub>2</sub>O under “usual conditions” prevailing in producer gas is, however, practically excluded. ZnO is reducible to metallic Zn only at extreme reducing conditions (gas composition with very low H<sub>2</sub>O and CO<sub>2</sub> content). Copper(I) oxide (Cu<sub>2</sub>O) in on the other hand easily reducible to metallic Cu at very low P<sub>H<sub>2</sub></sub>/P<sub>H<sub>2</sub>O</sub> ratio in syngas). Stability of Cu<sub>2</sub>O is improved in mixtures with TiO<sub>2</sub> or with some other stable metal oxides. NiO is reducible to Ni at higher temperatures under typical syngas composition. Reduction of Ce<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub> by syngas to metallic form of Ce and La is thermodynamically excluded.

**Table II:** Comparison of equilibrium concentrations of H<sub>2</sub>S for reactions of Zn, ZnO, Ni, NiO, Cu and Cu<sub>2</sub>O with H<sub>2</sub>S at supposed partial pressure of H<sub>2</sub>O vapors 0.1 bar and hydrogen pressure = 0.4 bar. The stable forms (in common raw producer gas) are marked in bold.

Reaction	H <sub>2</sub> S-equil. conc. at 500 K (bar)	H <sub>2</sub> S-equil. conc. at 700 K (bar)	H <sub>2</sub> S-equil. conc. at 900 K (bar)
Zn + H <sub>2</sub> S = ZnS + H <sub>2</sub>	2.00 E-17	4.91 E-12	5.86 E-09
<b>ZnO + H<sub>2</sub>S = ZnS + H<sub>2</sub>O</b>	<b>1.53 E-09</b>	<b>2.74 E-07</b>	<b>4.91 E-06</b>
<b>Ni + H<sub>2</sub>S = NiS + H<sub>2</sub></b>	<b>1.53 E-05</b>	<b>1.08 E-03</b>	<b>8,56 E-03</b>
NiO + H <sub>2</sub> S = NiS + H <sub>2</sub> O	6.88 E-09	8.23 E-07	9.72 E-06
<b>2Cu + H<sub>2</sub>S = Cu<sub>2</sub>S + H<sub>2</sub></b>	<b>1.90 E-06</b>	<b>4.93 E-05</b>	<b>2.42 E-04</b>
Cu <sub>2</sub> O + H <sub>2</sub> S = Cu <sub>2</sub> S + H <sub>2</sub> O	4.22 E-16	1.85 E-12	1.75 E-10

Producer gas from fluidized bed or fixed bed gasification of solid fuels with sulfur content can contain various organic sulfur compounds. According to general experience the most abundant organic sulfur compound in such a gas is thiophene. In the case of thiophene desulfurization reactions, the possible reaction outputs include water vapor, carbon (soot), benzene, CH<sub>4</sub>, alkenes, acetylene and other products. The majority of thiophene desulfurization reactions have very high equilibrium constant (resulting very low equilibrium P<sub>thiophene</sub>) – exceptions are mainly the reactions leading to formation of alkenes/alkanes. For two temperatures (800 and 1000 K), selected/assumed partial pressures of gas components (P<sub>H<sub>2</sub></sub> = 0.4 bar, P<sub>H<sub>2</sub>O</sub> = 0.1 bar, P<sub>CO</sub> = P<sub>CO<sub>2</sub></sub> = 0.2 bar and P<sub>CH<sub>4</sub></sub> = P<sub>Benzene</sub> = P<sub>Acetylene</sub> = P<sub>C<sub>2</sub>H<sub>4</sub></sub> = P<sub>butene</sub> = 0.01 bar) and two sorbents (Ce<sub>2</sub>O<sub>3</sub> and NiO) the equilibrium thiophene pressures are shown in **Table III**. The reactions with alkenes (ethylene and 1-butene) as products/reaction outputs are marked in bold.

The mechanism of thiophene reactions with metal oxides or metals (e.g. Ni) is relatively complicated involving physical sorption and formation of bonds with sulfur. The syngas components play a significant role and it is clear, that presence of higher concentration of benzene, alkenes and methane in gas causes higher concentrations of thiophene in gas. This is typical situation in co-gasification of coal or wood with plastics (PET, polypropylene etc.) It seems that the experimental experience is confirmed and explained also by thermodynamics.

**Table III:** Selected reactions of thiophene (C<sub>4</sub>H<sub>4</sub>S) with Ce<sub>2</sub>O<sub>3</sub> and NiO – equilibrium partial pressures of thiophene at 800 K and at 1000 K (P<sub>CO</sub> = P<sub>CO<sub>2</sub></sub> = 0.2 bar, P<sub>H<sub>2</sub></sub> = 0.4 bar, P<sub>H<sub>2</sub>O</sub> = 0.1 bar, P<sub>minorite</sub> = 0.01 bar)

Reaction	P <sub>thiophene</sub> at 800 K (bar)	P <sub>thiophene</sub> at 1000 K (bar)
Ce <sub>2</sub> O <sub>3</sub> + C <sub>4</sub> H <sub>4</sub> S + C <sub>2</sub> H <sub>2</sub> + H <sub>2</sub> = benzene + H <sub>2</sub> O(g) + Ce <sub>2</sub> O <sub>2</sub> S	2.66 E-17	3.15 E-12
NiO + C <sub>4</sub> H <sub>4</sub> S + C <sub>2</sub> H <sub>2</sub> + H <sub>2</sub> = benzene + H <sub>2</sub> O(g) + NiS	2.02 E-16	7.37 E-12
Ce <sub>2</sub> O <sub>3</sub> + C <sub>4</sub> H <sub>4</sub> S + 3H <sub>2</sub> = 2CH <sub>4</sub> + H <sub>2</sub> O(g) + 2C + Ce <sub>2</sub> O <sub>2</sub> S	2.81 E-23	5.00 E-18
NiO + C <sub>4</sub> H <sub>4</sub> S + 3H <sub>2</sub> = 2CH <sub>4</sub> + H <sub>2</sub> O(g) + 2C + NiS	2.14 E-22	1.17 E-17
<b>Ce<sub>2</sub>O<sub>3</sub> + C<sub>4</sub>H<sub>4</sub>S + 2H<sub>2</sub> + CO = 1-butene + CO<sub>2</sub> + Ce<sub>2</sub>O<sub>2</sub>S</b>	<b>1.55 E-07</b>	<b>8.51 E-04</b>
<b>NiO + C<sub>4</sub>H<sub>4</sub>S + 2H<sub>2</sub> + CO = 1-butene + CO<sub>2</sub> + NiS</b>	<b>1.18 E-06</b>	<b>1.99 E-03</b>
Ce <sub>2</sub> O <sub>3</sub> + C <sub>4</sub> H <sub>4</sub> S + ethylene = benzene + H <sub>2</sub> O(g) + Ce <sub>2</sub> O <sub>2</sub> S	1.78 E-12	7.95 E-10
NiO + C <sub>4</sub> H <sub>4</sub> S + ethylene = benzene + H <sub>2</sub> O(g) + NiS	1.35 E-11	1.86 E-09
Ce <sub>2</sub> O <sub>3</sub> + C <sub>4</sub> H <sub>4</sub> S = C <sub>2</sub> H <sub>2</sub> + H <sub>2</sub> O(g) + 2C + Ce <sub>2</sub> O <sub>2</sub> S	2.73 E-10	2.88 E-10
NiO + C <sub>4</sub> H <sub>4</sub> S = C <sub>2</sub> H <sub>2</sub> + H <sub>2</sub> O(g) + 2C + NiS	2.09 E-09	6.73 E-10
<b>Ce<sub>2</sub>O<sub>3</sub> + C<sub>4</sub>H<sub>4</sub>S + CO + 2H<sub>2</sub> = CO<sub>2</sub> + 2C<sub>2</sub>H<sub>4</sub> + Ce<sub>2</sub>O<sub>2</sub>S</b>	<b>1.22 E-09</b>	<b>3.07 E-07</b>
<b>NiO + C<sub>4</sub>H<sub>4</sub>S + CO + 2H<sub>2</sub> = CO<sub>2</sub> + 2C<sub>2</sub>H<sub>4</sub> + NiS</b>	<b>9.32 E-09</b>	<b>7.17 E-07</b>

For application of mixed sorbents for H<sub>2</sub>S/COS removal interactions of the oxide sorbents with other sulfides (competitive sorption) are important. The interaction of Ce<sub>2</sub>O<sub>3</sub> with ZnS, MnS, NiS and mutual interaction of NiS, MnS and Cu<sub>2</sub>S with ZnO are thermodynamically assessed in **Table IV**. The interactions are usually more significant at lower temperatures (e.g. 600 K). Stability of MnS in presence of ZnO and Ce<sub>2</sub>O<sub>3</sub> is weak. Stability of Cu<sub>2</sub>S in mixture with ZnO depends extremely on presence of hydrogen and water vapor in gas (ratio of P<sub>H<sub>2</sub></sub>/P<sub>H<sub>2</sub>O</sub>). Ce<sub>2</sub>O<sub>3</sub> can pull the sulfur out from MnS, NiS and even ZnS. In reality those solid-solid reactions run with sufficient speed only at temperatures over the Taman temperature when the crystal lattice is more pliant/movable.

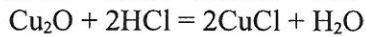
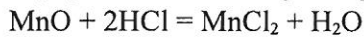
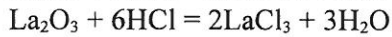
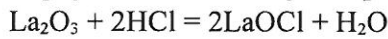
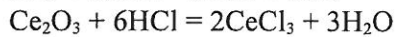
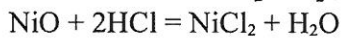
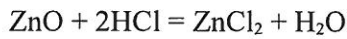
**Table IV:** Thermodynamic equilibria in solid-solid reactions among Ce<sub>2</sub>O<sub>3</sub> and other sulfides, ZnO and other sulfides and one reaction involving also hydrogen at 600 K and 1000 K

Reaction	Δ G <sub>r</sub> (kJ/mol)		K <sub>eq</sub> (-)	
	600 K	1000 K	600 K	1000 K
ZnS + Ce <sub>2</sub> O <sub>3</sub> = ZnO + Ce <sub>2</sub> O <sub>2</sub> S	-22.495	-2.665	90.87	1.37
MnS + Ce <sub>2</sub> O <sub>3</sub> = MnO + Ce <sub>2</sub> O <sub>2</sub> S	-45.527	-24.063	9196.5	18.07
NiS + Ce <sub>2</sub> O <sub>3</sub> = NiO + Ce <sub>2</sub> O <sub>2</sub> S	-29.039	-7.068	337.41	2.33
NiS + ZnO = NiO + ZnS	-6.544	-4.403	3.71	1.69
MnS + ZnO = ZnS + MnO	-23.032	-21.398	101.2	13.11
Cu <sub>2</sub> S + ZnO = ZnS + Cu <sub>2</sub> O	65.894	80.353	1.83 E-06	6.35 E-05
Cu <sub>2</sub> S + ZnO + H <sub>2</sub> = ZnS + 2Cu + H <sub>2</sub> O(g)	-23.252	-16.853	105.76	7.59

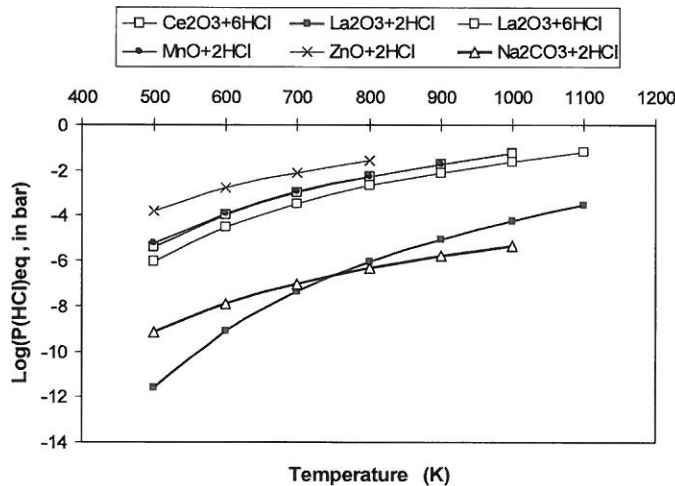
### Dehalogenation of syngas (removal of HCl and HF) by desulfurization sorbents

If the producer gas (syngas) contains HCl and HF, generally the sulfur sorbents can react with them. In the case of reactions of hydrogen chloride the following reactions have been assumed:

The products of the reactions of HCl with the metal oxides sorbents (primarily intended for sulfur removal) are generally corresponding chlorides. Only in the case of  $\text{La}_2\text{O}_3$  two products have been taken into consideration: lanthanum oxy-chloride ( $\text{LaOCl}$ ) and lanthanum(III) chloride ( $\text{LaCl}_3$ ):



The computed equilibrium HCl pressures are shown in **Fig. 3**, where they are compared with equilibrium HCl pressure in reaction of classic HCl sorbent (soda):



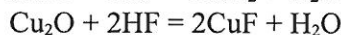
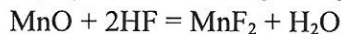
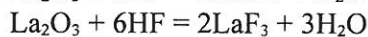
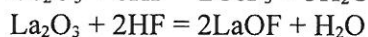
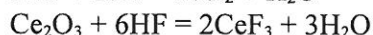
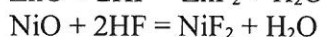
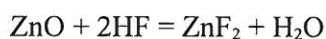
**Fig. 3:** Dependence of equilibrium HCl pressures on temperature for ZnO, MnO, NiO,  $\text{La}_2\text{O}_3$  and  $\text{Ce}_2\text{O}_3$  solid sorbents (assumed  $P_{\text{H}_2\text{O}} = 0.1$  bar,  $P_{\text{CO}_2} = 0.2$  bar)

The values of equilibrium pressures of HCl in the case of  $\text{Cu}_2\text{O}$  reaction are in a region between the reactions of  $\text{La}_2\text{O}_3$  with HCl and for NiO the  $(P_{\text{HCl}})_{\text{eq}}$  are slightly above the equilibrium



pressures of HCl for ZnO sorbent. As it follows from the Fig. 3 practically only the  $\text{La}_2\text{O}_3$  sorbent (under conditions of LaOCl formation) can remove efficiently HCl at temperatures below approx. 800 K. The  $\text{Cu}_2\text{O}$  sorbents can remove efficiently HCl (it means equil.  $P_{\text{HCl}} < 10^{-6}$  bar) only at temperatures approx. below 600 K. ZnO, NiO, MnO and  $\text{Ce}_2\text{O}_3$  sorbents have weaker equilibrium sorption of HCl (inapplicable for realistic conditions of syngas cleaning).

For removal of hydrogen fluoride (HF) from syngas the following reactions have been thermodynamically analyzed:



Similarly as for the reactions of  $\text{La}_2\text{O}_3$  with HCl two products of reaction with HF have been assumed: lanthanum oxy-fluoride (LaOF) and lanthanum(III) fluoride ( $\text{LaF}_3$ ).

The computed equilibrium HF pressures are shown in Fig. 4, where they are compared with equilibrium HF pressure in reaction of classic HCl sorbent (soda):

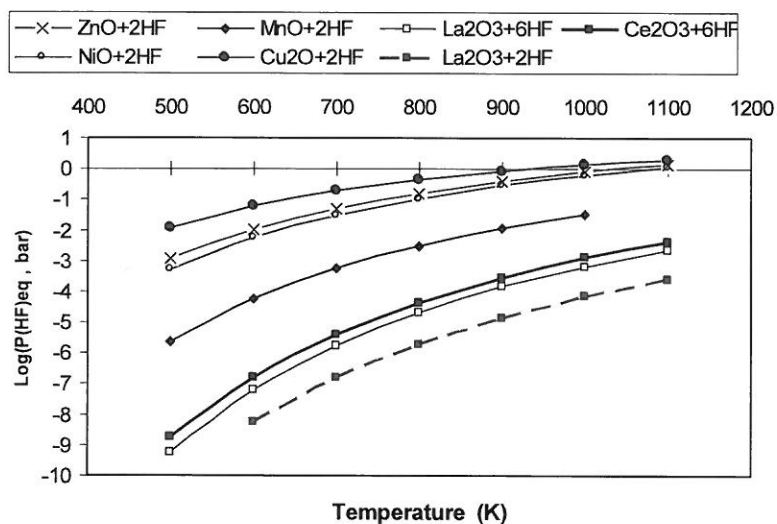


Fig. 4: Dependence of equilibrium HF pressures on temperature for ZnO, MnO, NiO,  $\text{Cu}_2\text{O}$ ,  $\text{La}_2\text{O}_3$  and  $\text{Ce}_2\text{O}_3$  solid sorbents (assumed  $P_{\text{H}_2\text{O}} = 0.1$  bar,  $P_{\text{CO}_2} = 0.2$  bar)

As it is obvious (Fig. 4) only the  $\text{La}_2\text{O}_3$  and  $\text{Ce}_2\text{O}_3$  based sorbents have ability to remove efficiently HF from gases (equil.  $P_{\text{HF}} < 10^{-6}$  bar) at temperatures below approx. 700-750 K. The  $\text{ZnO}$ ,  $\text{Cu}_2\text{O}$  and  $\text{NiO}$  based sorbents are inefficient in HF sorption.

### Interferences caused by HCl and HF in gas desulfurization ( $\text{H}_2\text{S}$ sorption)

For the HCl caused interference in gas desulfurization the following reactions were taken into consideration in thermodynamic analyses:

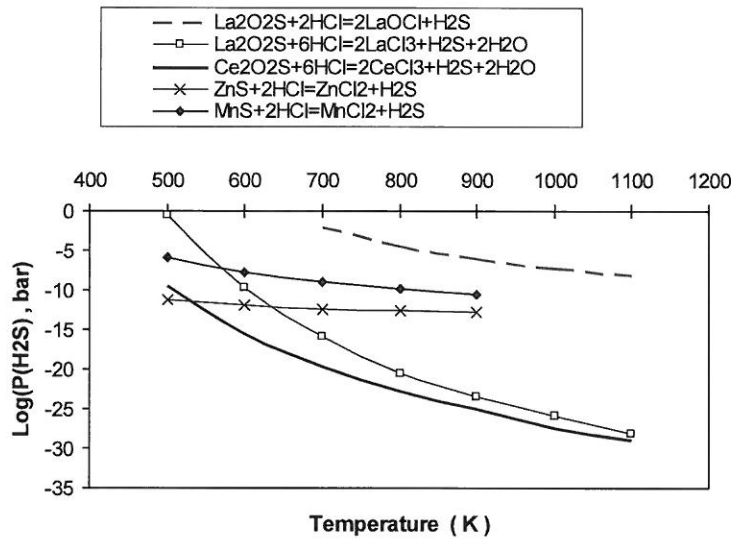
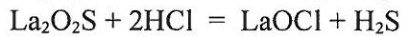
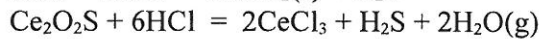
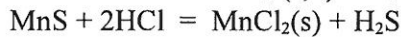
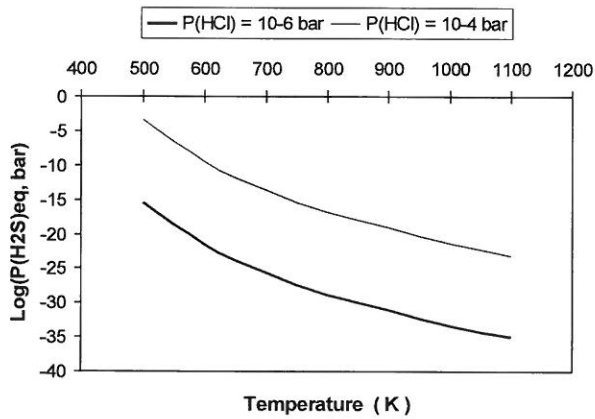


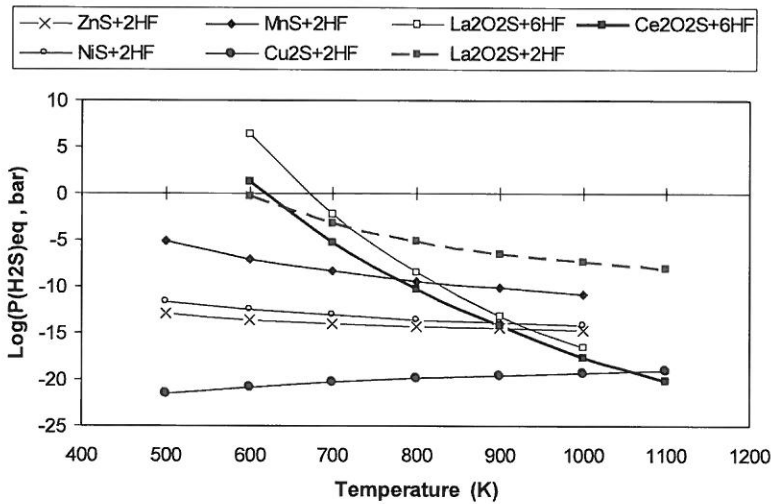
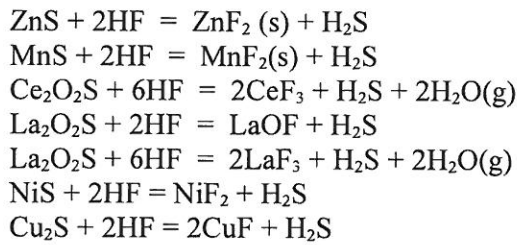
Fig. 5: Dependence of equilibrium  $\text{H}_2\text{S}$  pressures (expressed as  $\log(P_{\text{H}_2\text{S}} - \text{in bar})$ ) on temperature in reactions of selected sulfides with HCl ( $P_{\text{H}_2\text{O}} = 0.1$  bar,  $P_{\text{HCl}} = 10^{-5}$  bar)

The equilibrium  $\text{H}_2\text{S}$  pressures for reaction of  $\text{Cu}_2\text{S}$  with HCl are between  $(P_{\text{H}_2\text{S}})_{\text{eq}}$  for reactions of  $\text{ZnS}$  and  $\text{MnS}$  with HCl. The equil.  $P_{\text{H}_2\text{S}}$  pressures in reaction of  $\text{NiS}$  with HCl are similar to  $(P_{\text{H}_2\text{S}})_{\text{eq}}$  in reaction of  $\text{ZnS}$  with HCl. The strongest interference of HCl in desulfurization is found for  $\text{La}_2\text{O}_3$ , but only for reaction with HCl leading to  $\text{LaOCl}$  formation. Therefore the  $\text{La}_2\text{O}_3/\text{La}_2\text{O}_2\text{S}$  based sorbents of  $\text{H}_2\text{S}$  could be ineffective in gases with concentrations of HCl above approx. 5 ppm<sub>v</sub>. On the other hand the  $\text{ZnO}/\text{ZnS}$  and  $\text{Ce}_2\text{O}_3/\text{Ce}_2\text{O}_2\text{S}$  based sorbents are resistant to interferences of HCl in gas desulfurization ( $\text{H}_2\text{S}$  sorption). However, for the cerium oxide/oxy-sulfide based sorbents, very strong dependence of interferences on HCl concentration (proportional to  $(P_{\text{HCl}})^6$ ) has to be taken into account – as it is shown in Fig. 6



**Fig. 6** : Effect of  $P_{HCl}$  on dependence of equilibrium  $H_2S$  pressures on temperature for the reaction  $Ce_2O_2S + 6 HCl = 2CeCl_3 + 2H_2O + H_2S$  (assumed  $P_{H_2O} = 0.1$  bar).

Interferences in gas desulfurization caused by presence of HF in syngas have been analyzed for the following reactions:



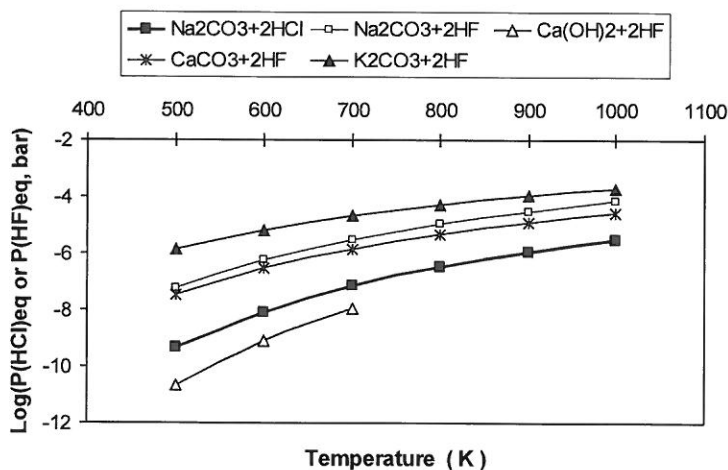
**Fig. 7 :** Dependence of equilibrium  $H_2S$  pressures (expressed as  $\log(P_{H_2S}$  - in bar)) on temperature in reactions of sulfides with HF ( $P_{H_2O} = 0.1$  bar,  $P_{HF} = 10^{-5}$  bar)

Presence of low HF concentration in syngas has very significant effect on efficiency of  $H_2S$  sorption mainly for  $La_2O_3/La_2O_2S$  and  $Ce_2O_3/Ce_2O_2S$  sorbents, partially on  $MnO/MnS$  sulfur sorbents. The cerium based sorbents are suitable for desulfurization in gases with some HF content rather at temperatures over 800 K. The Cu, Zn and Ni based sorbents do not suffer from interferences from the side of HF in gas desulfurization.

### Removal of HCl and HF by $Na_2CO_3$ , $K_2CO_3$ and calcium based sorbents

$Na_2CO_3$ ,  $K_2CO_3$  and partly calcium based sorbents are suitable for removal of HCl from gases at temperatures approx. 500- 900 K. Higher temperatures are unsuitable for soda and  $K_2CO_3$  based sorbents because at temperatures over approx. 900 K formation of eutectics with melting points below 1000 K should be expected. At water vapor and  $CO_2$  concentrations between 5 and 20 vol. % the attainable equilibrium concentrations of HCl are below 1 ppm<sub>v</sub> [22].  $K_2CO_3$  is a more efficient sorbent than the soda based sorbents. With  $K_2CO_3$  (theoretically) HCl concentrations in gas lower than approx. 10 ppb<sub>v</sub> are attainable.

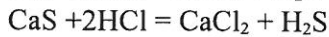
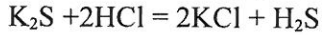
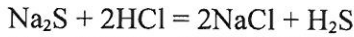
Situation in HF equilibrium sorption is different from HCl sorption by the alkali sorbents (**Fig. 8**): the  $Na_2CO_3$  and  $K_2CO_3$  sorbents are generally worse than calcium compounds based sorbents (e.g.  $Ca(OH)_2$  and  $CaCO_3$ ). With  $Na_2CO_3$  sorbents the HF concentrations lower than 1 ppm<sub>v</sub> are theoretically attainable only at temperatures below 600 K and at low  $H_2O$  and  $CO_2$  concentrations.  $K_2CO_3$  is even excluded for such gas cleaning (de-HF) requirements. The Ca-based sorbents (both calcium hydroxide and calcium carbonate) show better results in HF equilibrium removal from gas phase in a temperature range 500 – 900 K (**Fig. 8**).



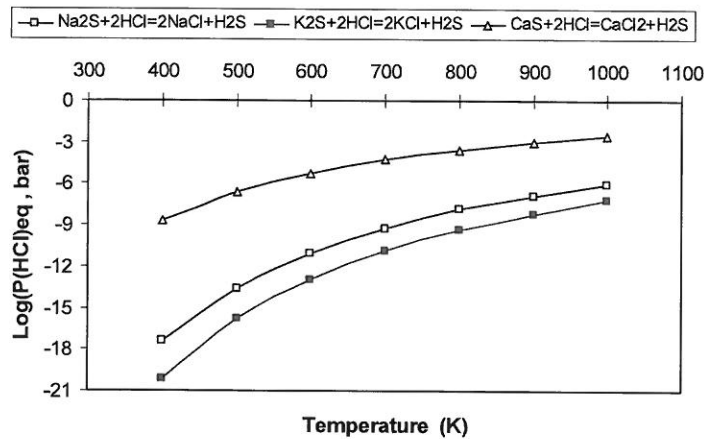
**Fig. 8:** Dependence of equilibrium HF or HCl concentrations (expressed as  $\log(P_{HF}$  - in bar) or  $\log(P_{HCl}$  - in bar)) on temperature for  $Na_2CO_3$ ,  $K_2CO_3$ ,  $Ca(OH)_2$  and  $CaCO_3$  based sorbents ( $P_{H_2O} = P_{CO_2} = 0.1$  bar)

### Interferences caused by H<sub>2</sub>S presence in HCl and HF removal by alkali-sorbents

For the thermodynamic study of H<sub>2</sub>S interferences in HCl sorption reaction the following reactions have been assumed:

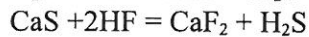
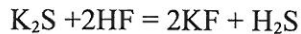
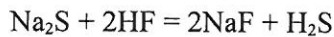


The results of computations of equilibrium HCl pressures under assumption of  $P_{\text{H}_2\text{S}} = 0,001$  bar are shown in **Fig. 9**. As clearly visible, the HCl sorption by Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> sorbents enables at presence of 1000 ppm<sub>v</sub> of H<sub>2</sub>S still attaining of equilibrium HCl concentrations in gas below approx. 1 ppb<sub>v</sub> at temperature below 700 K.

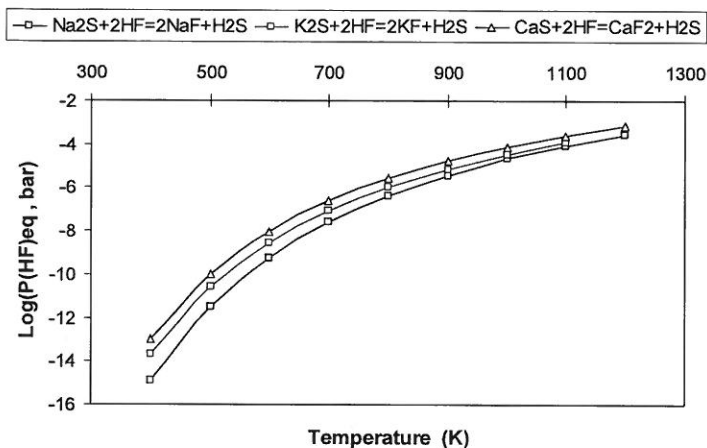


**Fig. 9:** Interference of H<sub>2</sub>S in sorption of HCl by alkali sorbents expresses as dependence of equilibrium HCl pressures in indicated reaction systems with  $P_{\text{H}_2\text{S}} = 10^{-3}$  bar

Another situation is in HF sorption in presence of higher concentrations (partial pressures) of H<sub>2</sub>S. For a similar system of reactions as in the case of HCl sorption:



The results of computations of equilibrium HF pressures at  $P_{\text{H}_2\text{S}} = 0.001$  bar are shown in **Fig. 10**. The equilibrium concentrations of HF lower than approx. 1 ppb<sub>v</sub> can be attained only at low temperatures (approx. for  $T < 600$  K) and rather with Na<sub>2</sub>CO<sub>3</sub>/Na<sub>2</sub>S based sorbents. On the other hand the calcium hydroxide based sorbents are less sensitive on H<sub>2</sub>S presence in HF removal than in HCl sorption.



**Fig. 10:** Interference of H<sub>2</sub>S in sorption of HF by alkali sorbents expresses as dependence of equilibrium HF pressures in indicated reaction systems with  $P_{\text{H}_2\text{S}} = 10^{-3}$  bar

#### 4. Conclusions

Ce<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub> based sorbents of sulfur compounds (H<sub>2</sub>S COS, thiophene) are at least comparable with ZnO based sorbents at temperatures between 600 and 800 K. MnO is the less suitable H<sub>2</sub>S sorbent. CeO<sub>2</sub> is not suitable sorbent of sulfur compounds at all and must be used only in a pre-reduced state (Ce<sub>x</sub>O<sub>y</sub>). Ce<sub>2</sub>O<sub>3</sub> enables theoretically (similarly as Cu<sub>2</sub>O) achievement of H<sub>2</sub>S equilibrium concentrations lower than 1 ppb-v in gas at temperatures below 600 K. Copper(I) oxide (Cu<sub>2</sub>O) could be a very efficient H<sub>2</sub>S sorbent, but due to easy reduction of Cu<sub>2</sub>O in syngas to less efficient elemental Cu, its applicability is thermodynamically weaker in comparison with ZnO or Ce<sub>2</sub>O<sub>3</sub>. Deepness of removal of thiophene and similar organic sulfur compounds depends on presence of mainly higher alkenes/alkanes (propene/propane, butane/butane, ethylene, etc.) in gas. With their higher concentrations, it seems, the equilibrium thiophene concentrations increase. The other removal/destruction reactions of thiophene (e.g. by means of Ce<sub>2</sub>O<sub>3</sub> or NiO) indicate thermodynamic viability of its very deep removal from syngas.

Applicability of mixed (binary, ternary) sorbents of sulfur compounds is influenced by interactions of the formed sulfides with metal oxides present. The interactions are usually more significant at lower temperatures (e.g. 600 K). Stability of MnS in presence of ZnO and Ce<sub>2</sub>O<sub>3</sub> is weak. Stability of Cu<sub>2</sub>S in mixture with ZnO depends extremely on presence of hydrogen and water vapor in gas (ratio of  $P_{\text{H}_2}/P_{\text{H}_2\text{O}}$ ). Cerium oxide (Ce<sub>2</sub>O<sub>3</sub>) can pull the sulfur out from MnS, NiS and even from ZnS. In reality, however, those solid-solid reactions run with sufficient speed only at higher temperatures (over the Tamam temperature).

Reactions of HCl and HF with sulfur sorbents can be significant mainly at lower temperatures. Practically only the La<sub>2</sub>O<sub>3</sub> sorbent (under conditions of LaOCl formation) can remove efficiently HCl at temperatures below approx. 800 K. The Cu<sub>2</sub>O sorbents can remove efficiently HCl (it means equilibrium  $P_{\text{HCl}} < 10^{-6}$  bar) only at temperatures approx. below 600 K. ZnO, NiO, MnO and Ce<sub>2</sub>O<sub>3</sub> sorbents have weaker equilibrium sorption of HCl (inapplicable for realistic conditions of syngas cleaning). In HF removal by the studied sorbents, similarly as for the

reactions of  $\text{La}_2\text{O}_3$  with HCl, two products of reaction with HF are realistically possible: lanthanum oxy-fluoride (LaOF) and lanthanum(III) fluoride ( $\text{LaF}_3$ ). Only the  $\text{La}_2\text{O}_3$  and  $\text{Ce}_2\text{O}_3$  sorbents have ability to remove efficiently HF from gases (equilibrium  $P_{\text{HF}} < 10^{-6}$  bar) at temperatures below approx. 750 K. The ZnO,  $\text{Cu}_2\text{O}$  and NiO based sorbents are inefficient in HF sorption from syngas.

Interferences of HCl and HF in  $\text{H}_2\text{S}$  removal reactions are not important in the case of ZnO. Conditions preferring formation of LaOCl or LaOF (higher  $\text{H}_2\text{O}$  concentrations in gas, lower temperatures) exclude the La-based sorbents of  $\text{H}_2\text{S}$ , because of significant interference in sorption from the side of HCl and HF.

The strongest interference of HCl in desulfurization (removal of  $\text{H}_2\text{S}$  from gas) was found for  $\text{La}_2\text{O}_3$ , but only for reaction with HCl leading to LaOCl formation. Therefore the  $\text{La}_2\text{O}_3/\text{La}_2\text{O}_2\text{S}$  based sorbents of  $\text{H}_2\text{S}$  could be ineffective for desulfurization in gases with concentrations of HCl above approx. 5 ppm<sub>v</sub>. On the other hand, the ZnO/ZnS and  $\text{Ce}_2\text{O}_3/\text{Ce}_2\text{O}_2\text{S}$  based sorbents are resistant to interferences of HCl in gas desulfurization ( $\text{H}_2\text{S}$  sorption). However, for the cerium oxide/oxy-sulfide based sorbents, very strong dependence of interferences on HCl concentration (proportional to  $(P_{\text{HCl}})^6$ ) has to be taken into account. At temperatures over 600 K  $\text{Ce}_2\text{O}_3$  based sorbents exert the lowest attainable equilibrium concentration of  $\text{H}_2\text{S}$ , however presence of HCl in gas has tremendous effect on attainable equilibrium concentrations of  $\text{H}_2\text{S}$ . Interference of HF is even worse than the HCl effects in gas desulfurization. The  $\text{Ce}_2\text{O}_3$  and  $\text{La}_2\text{O}_3$  sorbents are not applicable in such a case at temperatures below 800 K. On the other hand interferences of HF in ZnS formation and  $\text{H}_2\text{S}$  sorption are weaker than the effects of HCl.

Presence of low HF concentration in syngas has very significant effects on efficiency of  $\text{H}_2\text{S}$  sorption mainly for  $\text{La}_2\text{O}_3/\text{La}_2\text{O}_2\text{S}$  and  $\text{Ce}_2\text{O}_3/\text{Ce}_2\text{O}_2\text{S}$  sorbents, partially on MnO/MnS sulfur sorbents. The cerium based sorbents are suitable for desulfurization in gases with some HF content rather at higher temperatures over 800 K. The Cu, Zn and Ni based sorbents do not suffer from interferences from the side of HF in gas desulfurization.

Hydrogen chloride can be removed at temperatures between approx. 500 and 900 K by soda and  $\text{K}_2\text{CO}_3$  based sorbents. With  $\text{K}_2\text{CO}_3$  it is possible to attain equilibrium concentrations of HCl in gas on a level of 10 ppb<sub>v</sub>. The equilibrium sorption of HF by alkaline sorbents presents a more complicated matter. The common alkali carbonates ( $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$ ) are surprisingly less suitable for removal of HF than the calcium based sorbents ( $\text{Ca}(\text{OH})_2$  and  $\text{CaCO}_3$ ). The otherwise reactive  $\text{K}_2\text{CO}_3$  sorbent is unable to remove HF from syngas on a level around 1 ppm<sub>v</sub>. Attaining of HF concentration in gas below approx. 10 ppb<sub>v</sub> is possible only by means of  $\text{Ca}(\text{OH})_2$  or CaO based sorbents at temperatures below 650 – 700 K. The interferences of  $\text{H}_2\text{S}$  in dehalogenation (de-HCl and de-HF) of syngas by soda and  $\text{K}_2\text{CO}_3$  based sorbents are generally more important in HF removal.

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