Stability of lanthanum oxide-based H$_2$S sorbents in realistic fuel processor/fuel cell operation

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ABSTRACT

We report that lanthana-based sulfur sorbents are an excellent choice as once-through chemical filters for the removal of trace amounts of H$_2$S and COS from any fuel gas at temperatures matching those of solid oxide fuel cells. We have examined sorbents based on lanthana and Pr-doped lanthana with up to 30 at.% praseodymium, having high desulfurization efficiency, as measured by their ability to remove H$_2$S from simulated reformate gas streams to below 50 ppbv with corresponding sulfur capacity exceeding 50 mg S g$_{sorbent}$$^{-1}$ at 800 °C. Intermittent sorbent operation with air-rich boiler exhaust-type gas mixtures and with frequent shutdowns and restarts is possible without formation of lanthanide oxycarbonate phases. Upon restart, desulfurization continues from where it left at the end of the previous cycle. These findings are important for practical applications of these sorbents as sulfur polishing units of fuel gases in the presence of small or large amounts of water vapor, and with the regular shutdown/start-up operation practiced in fuel processors/fuel cell systems, both stationary and mobile, and of any size/scale.

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1. Introduction

Among the advanced power generation technologies, molten carbonate fuel cell (MCFC) and solid oxide fuel cell (SOFC) systems, have received a lot of attention due to their increased thermal efficiency and reduced environmental impact compared to conventional energy generators. The hydrogen-rich gas mixture obtained from fuel conversion in an autothermal or steam reformer reactor or from a coal gasifier is used to power these fuel cells. However, to protect the nickel-based anode electrocatalyst from sulfur, a sorbent material must be used. Even low sulfur fuels will produce tens of ppmv H$_2$S at the reformer exit, while the levels of H$_2$S in gasifier-exit gases may be over 1000 ppmv.

Lanthanide oxides and their mixtures are very efficient sorbents of H$_2$S at temperatures compatible with high-temperature fuel cells, i.e. 650–800 °C, removing sulfur to sub-ppm levels [1,2]. The lanthanide oxides are unique in that they possess the highest H$_2$S removal efficiency among all oxide sorbents in any reformate gas mixture, with high or low H$_2$O content, as can be calculated from thermodynamics [3–5]. While the bulk sorbent regeneration is difficult [2,6,7], we recently discovered that these

materials, even when sulfided, have additional regenerative surface adsorption capacity for H$_2$S [1,3,8,9]. Hence, they can be used in compact sorbers upstream of an SOFC to remove the H$_2$S. The saturated surface is periodically regenerated by a purge gas [1].

A different approach may be advantageous in some fuel cell applications, whereby a once-through filter is used to collect trace amounts of sulfur and protect the fuel cell. In such cases, periodic replacement of the filter house with fresh sorbent will be required. The unparalleled sulfur efficiency and high sulfur capacity of mixed lanthanide oxide sorbents at 800 °C makes them an excellent choice as high-temperature sulfur guard beds. In practical applications of these sorbent filters, frequent start-ups and shutdowns may be required. During shutdown, the sorbent should exhibit durability in the presence of condensing water vapor. In the context of sustainable plant design, it is desirable to improve thermal efficiency by the use of available secondary process gas streams to heat up the desulfurization unit. Fig. 1 shows a possible operation scheme where the boiler exhaust gas is used to heat the sorbent bed to the desired operation temperature.

In this paper, we examine the stability and durability of bulk lanthanide oxide sorbents in start-up and intermittent operation, with air, H$_2$O, and CO$_2$-containing gases, and the impact that such treatments have on the absorption capacity and efficiency of these sorbents when used as high-temperature sulfur guard beds upstream of fuel cells.

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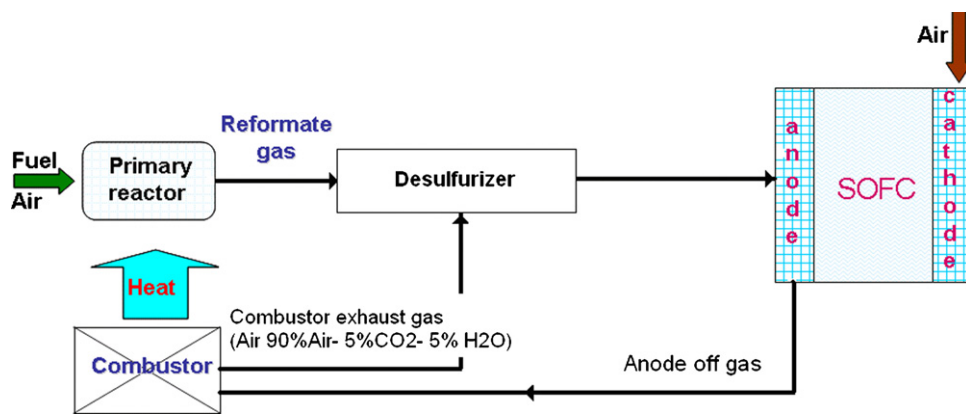(M. Flytzani-Stephanopoulos).

Fig. 1. Integrated operation scheme where combustor exhaust gas is used to heat up the desulfizer.

2. Experimental

2.1. Sorbent preparation and characterization

All samples tested here were prepared by a variation of the urea coprecipitation/gelation method (UGC) [10], as adapted previously in our laboratory [11]. For the preparation of 30 at.% praseodymium-doped lanthanum oxide, 22.73 g lanthanum (III) nitrate hydrate 99.9% (Aldrich), and 9.79 g praseodymium (III) nitrate hexahydrate 99.9% (Aldrich) were mixed and dissolved in 600 mL of deionized (DI) water. This gives a La/Pr atomic ratio of 7:3. Excess urea (72 g) was added into the solution under constant stirring and boiling over a hot plate. Once precipitation occurred, DI water was added to 800 mL, and the solution was kept boiling for 8 h. The precipitate was filtered, washed twice, dried at 120 °C overnight and eventually crushed to a powder with particle size <53 μm. Samples were typically calcined to 650 °C in air at a rate of 2 °C min^{-1} and then held at the final temperature for 4 h. A few samples were calcined at 800 °C.

The sorbent BET surface areas were measured by single-point N$_2$ adsorption/desorption cycles using a Micromeritics model AutoChem II 2920 apparatus. X-ray diffraction (XRD) patterns were obtained using a Rigaku Model RU300 instrument with a rotating anode generator and a monochromatic detector. Cu Kα$_1$ radiation was used, with a power setting of 50 kV and 300 mA.

2.2. Sorbent sulfidation tests

Sulfidation tests were performed at atmospheric pressure in a packed-bed quartz-tube microreactor (inner diameter of 1.0 cm) to evaluate the sorbent H$_2$S removal efficiency and sulfur capacity at 1 ppm H$_2$S breakthrough. Particles with a diameter of <53 μm were used in the reactivity tests. All gas mixtures used were of analytical grade (H$_2$S (Airgas, 99.5/0.1 He/H$_2$S), H$_2$ (Airgas, 50/50 H$_2$/He), CO (Airgas, pure), CO$_2$ (Airgas, pure), helium (Airgas, 99.999%), air (Airgas, dry air)).

The samples were first heated to the desired sulfidation temperature at a heating rate of 40 °C min^{-1} and left for 30 min at temperature with a gas mixture containing 90% air–5% CO$_2$–5% H$_2$O, simulating the composition of a practical combustor exhaust gas stream. The sulfidation gas mixture, simulating a realistic reformate gas composition from autothermal reforming of a liquid fuel (250 ppm H$_2$S–20% H$_2$–25% CO–5% CO$_2$–5% H$_2$O–bal. gas), was then introduced. The balance gas used was He rather than N$_2$ as the former is the typical balance gas of all gases used in our lab.

Two different space velocities and therefore contact time values were examined; a flow rate of 200 mL min^{-1} (NTP) and 0.48 g sorbent was used for the low space velocity (25,000 h^{-1}) tests, and a flow rate of 300 mL min^{-1} (NTP) combined with 0.1 g sorbent was employed for the high space velocity (180,000 h^{-1}) tests. H$_2$S and SO$_2$ concentrations in the exit gas were measured on-line, using a Western Research Series 900 UV–Vis analyzer (Ametek). Measurements of sub-ppm concentrations of H$_2$S and of COS were followed by a Shimatzu GC-2014 equipped with a FPD detector.

3. Results and discussion

3.1. Carbonate formation and decomposition

The option of using the combustor off gas for sorbent pretreatment is of practical importance not only because of better heat integration, but also because of a potential issue of lanthanide carbonate and oxycarbonate formation in this type gas. If this occurs, the temperature for carbonate decomposition in the same gas mixture must be established.

Initially, lanthanum oxide-based sorbents prepared by the UGC method and calcined in air at 650 °C do contain oxycarbonates, as identified by XRD analysis. This is shown in Table 1 for the fresh as prepared materials containing lanthanum and praseodymium
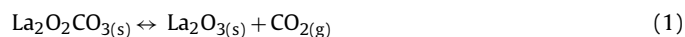
Table 1
Characterization of as prepared sorbents[a].

Sample	Particle size (nm)[b]	BET surface area (m^2 g^{-1})	XRD-identified phases		Surface area of pretreated sample (m^2 g^{-1})	XRD-identified phases in pretreated samples
Ce(30% La)O$_x$	7.5	85	CeO$_2$	La$_2$O$_2$CO$_3$	28[c]	CeO$_2$
La$_2$O$_3$	44.4	5	La$_2$O$_3$	La$_2$O$_2$CO$_3$	4[c]	La$_2$O$_3$
La$_{0.7}$Pr$_{0.3}$O$_x$	16.3	4	La(Pr)$_2$O$_2$CO$_3$		3.7[d]	La(Pr)$_2$O$_2$CO$_3$

[a] Material calcined at 650 °C, in air, 4 h.
[b] From the Scherrer's equation $D = (K \times \lambda)/(\beta \times \cos(\theta))$; $K = 0.9$, $\lambda = 0.154$ nm, β and θ are the width and center of XRD peak studied.
[c] Pretreatment at 800 °C for 1 h in 50% H$_2$–10% H$_2$O–He.
[d] Pretreatment at 600 °C for 30 min in 90% air–5% CO$_2$–5% H$_2$O.

Table 2
CO_2 equilibrium concentrations[*].

CO_2 concentration [%]					
Temperature [°C]	Composition 1[a]	Composition 2[b]	Composition 3[c]	Composition 4[d]	Carbonate decomposition[e]
600	0	1.68	12.0	5	0.3
700	0	1.56	6.8	5	2.6
800	0	1.22	5.6	5	14

[a] 50% H_2–10% H_2O–He bal.
[b] 50% H_2–10% H_2O–5% CO_2–He bal.
[c] 20% H_2–25% CO–5% CO_2–5% H_2O–He bal.
[d] 90% Air–5% H_2O–5% CO_2.
[e] Calculated from ref. [15]: $\ln P_{CO_2}$ (Pa) $(\pm0.22) = -17502.2/T + 25.87$ $(773 \leq T (K) \leq 1190)$.
[*] Calculated with the NASA Computer software program CEA (Chemical Equilibrium with Applications).

oxides; ceria does not form a stable carbonate above 500 °C. This is in agreement with literature reports of the stability of these carbonates [12–17].

Carbonate formation can result from adventitious carbon in air, but it can also be due to the method of preparation. In the UGC method, in the basic solution resulting from the urea decomposition, carbonate ions and ammonia are formed. The calcination temperature of 650 °C is not enough to fully decompose the lanthanum oxycarbonate, as Table 1 shows.

On the basis of the thermodynamic equilibrium for the decomposition reaction in air:

$$La_2O_2CO_{3(s)} \leftrightarrow La_2O_{3(s)} + CO_{2(g)} \tag{1}$$

a gas with a partial pressure of CO_2 lower than 0.14 atm will allow the decomposition of the oxycarbonate at 800 °C, while decomposition will not take place at 650 °C, unless the CO_2 partial pressure is lower than 0.01 atm [16]. The equilibrium CO_2 concentrations for the carbonate decomposition at 600, 700 and 800 °C and the CO_2 gas phase equilibrium concentration for four gas mixtures of interest are listed in Table 2. In a practical application, where the combustor exhaust gas stream is used to heat up the sorbent, a typical CO_2 content is ~5%. This is enough to move the equilibrium to the left. It is therefore of practical interest to investigate whether carbonate formation, if it occurs, will adversely affect the sulfur uptake by the sorbent. Based on the literature [16,18–28], the temperature range of decomposition in pure CO_2 as measured by thermogravimetry and differential thermal analysis is 720–900 °C and 900–960 °C for $Pr_2O_2CO_3$ and $La_2O_2CO_3$, respectively.

At first, decomposition of the carbonate species was examined by heating the fresh sample up to 650 °C in a pure helium stream at a rate of 10 °C min^{-1}. The concentrations of H_2O, CO and CO_2 in the outlet gas were monitored on-line by a quadrupole mass spectrometer and the amounts of CO and CO_2 eluted during decomposition were found using calibration lines.
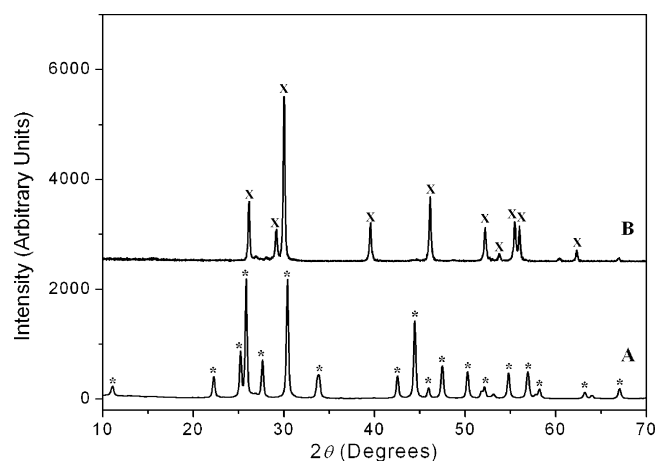
The as calcined sample is pure oxycarbonate and complete decomposition to the corresponding oxide is achieved upon treatment at 800 °C in 50% H_2–10% H_2O–He, as confirmed by X-ray diffraction analysis (Fig. 2). As shown in Fig. 3A, for lanthanum oxycarbonate, decomposition starts around 550 °C and proceeds slowly while the temperature is kept at the set value of 650 °C. Even after 1 h at 650 °C not all the CO_2 was removed; while complete carbonate decomposition should result in 0.33 mmol of CO_2 released, the amount measured by peak integration during the test was only 40% of the total value. An additional test was carried out, in which the sample was heated up to 800 °C (Fig. 3B). This time the amount of CO_2 eluted was ~0.37 mmol, corresponding to complete decomposition of the oxycarbonate to the oxide phase. When a 50% H_2–He mixture was used to reduce the carbonate, the main carbon oxide peak was from CO, not CO_2; concomitant consumption of H_2 and evolution of H_2O are indicative of the reverse water gas shift occurring over the sample (Fig. 3C). Similar results were obtained for the

fresh (calcined at 650 °C) 30 at.% praseodymium-doped lanthana, shown in Fig. 4A–C.
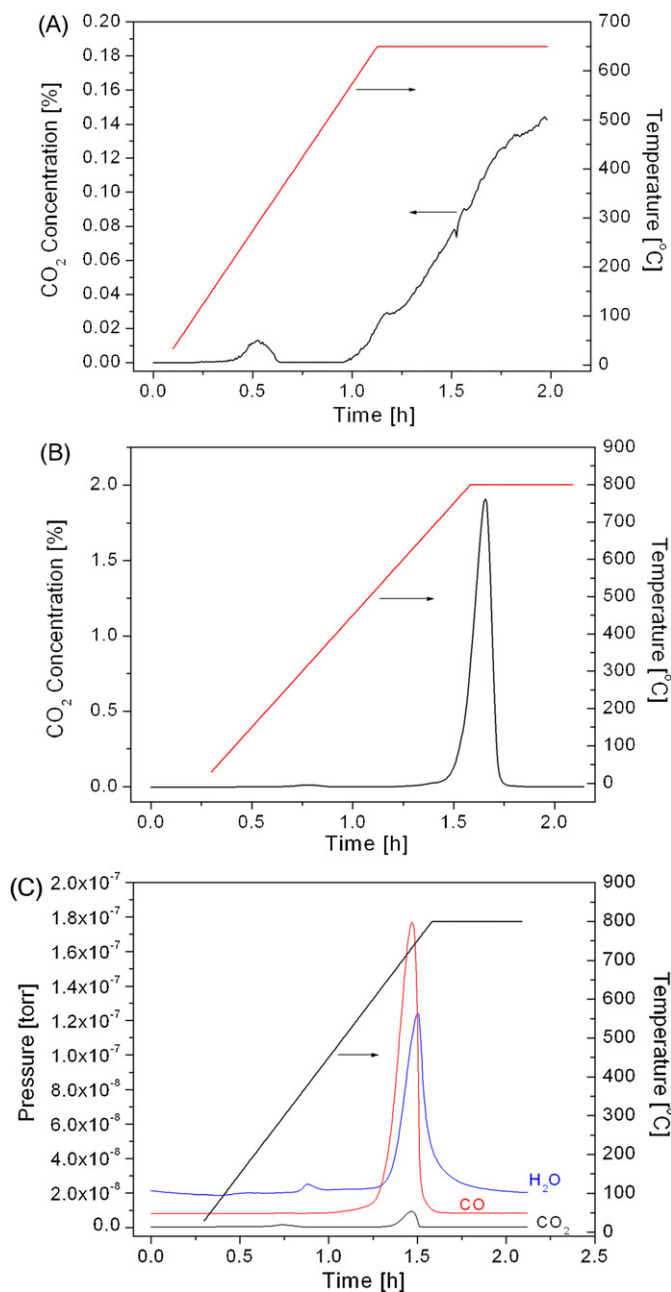
The effect of the air-rich mixture (90% air/5% CO_2/5% H_2O) on carbonate formation was then examined. First, the sample was heated up to 650 °C and after 30 min, cooled to RT always in the same gas mixture. The CO_2 concentration in the gas stream was stable around the set value of 5% throughout the duration of this step. Once RT was reached, the gas was switched to helium and the formation of carbonate species was examined once again by thermal decomposition up to 800 °C (Fig. 5). Indeed, carbonate had formed during the pretreatment step and integration of the area under the peak gave an approximate amount of 2.4 mmol of CO_2 g$_{sorbent}^{-1}$, which is around the stoichiometric amount resulting from complete decomposition of carbonate. The presence of carbonate species on the as calcined and exhaust gas-pretreated samples was confirmed also by the XRD patterns shown in Fig. 6A and B.

The amounts of CO_2 and CO eluted during thermal decomposition of the carbonate from the fresh and air-pretreated samples are summarized in Table 3. The values in parenthesis represent the degree of carbonation of the sample, defined as the moles of CO_2 eluted divided by the stoichiometric moles of CO_2 assuming decomposition of bulk oxycarbonate. The occurrence of reverse water gas shift reaction over lanthana and Pr-doped lanthana is also proven by the relative amounts of CO and CO_2 (Table 3), when the 50% H_2–He gas mixture was used. In fact, for both samples, approximately 85% of the total carbon released is due to CO and only 15% to CO_2.
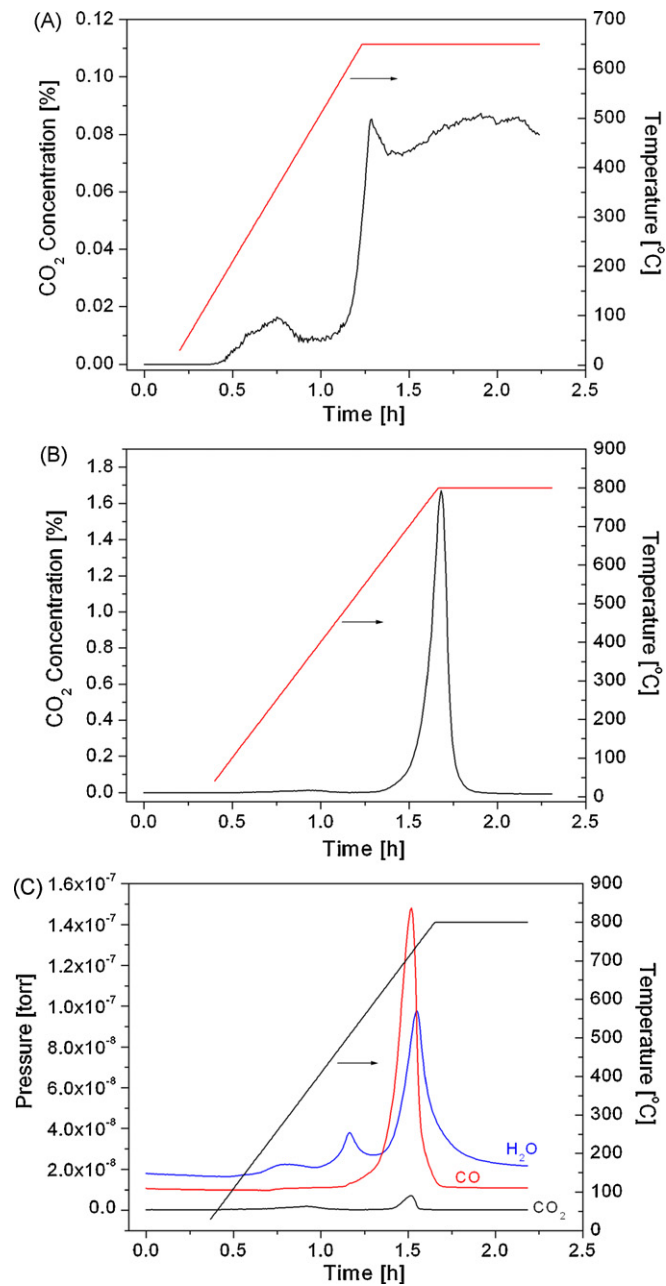
Comparison of the estimated CO_2 amounts released at the two different temperatures, found that an 800 °C-treatment step was necessary for the complete decomposition of the oxycarbonate to

Fig. 2. XRD pattern of as prepared La_2O_3 (Table 1); (A) after calcination in air at 650 °C for 4 h; (B) after pretreatment in 50% H_2–10% H_2O–He [(*) $La_2O_2CO_3$ Hexagonal, (x) La_2O_3 Hexagonal].

Fig. 3. Thermal decomposition of carbonate for La_2O_3 calcined at 650 °C; (A) heating to 650 °C and cooling He; (B) heating to 800 °C and cooling in He; (C) heating to 800 °C and cooling in 50% H_2–He.
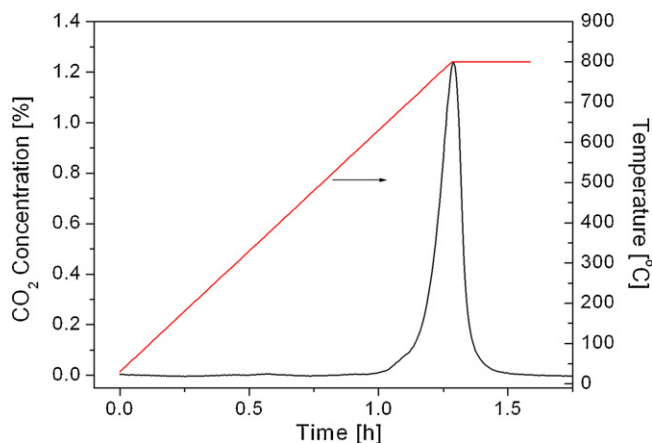
Fig. 4. Thermal decomposition of carbonate for $La_{0.7}Pr_{0.3}O_x$ calcined at 650 °C; (A) heating to 650 °C and cooling He; (B) heating to 800 °C and cooling in He; (C) heating to 800 °C and cooling in 50% H_2–He.

Table 3
Summary results of thermal decomposition of carbonate.

Decomposition conditions		Amount of CO_2 and/or CO eluted [mmol $g_{sorbent}^{-1}$]			
Gas composition	Temperature [°C]	La_2O_3		$La_{0.7}Pr_{0.3}O_x$	
		CO_2	CO	CO_2	CO
He	650	1.1 (40%)	0	1.2 (47%)	0
He	800	3.1 (100%)	0	3.1 (100%) 2.5 (94%)[a]	0
50% H_2–He	800	0.33 (12%)	2.3 (84%)[b]	0.37 (14%)	1.9 (72%)[b]

The values in the parenthesis represent the degree of carbonation of the sample.
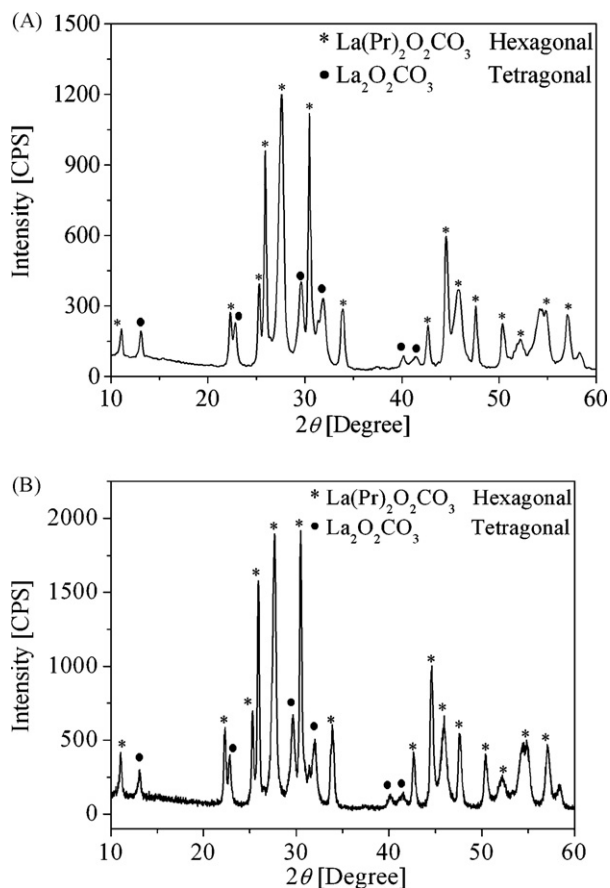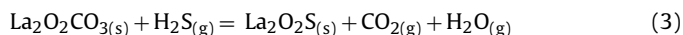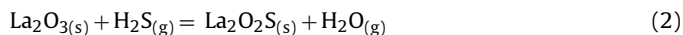[a] After pretreatment in 90% air–5% CO_2–5% H_2O at 650 °C for 30 min.
[b] Considering that CO is produced from CO_2 conversion by the reverse water gas shift reaction.
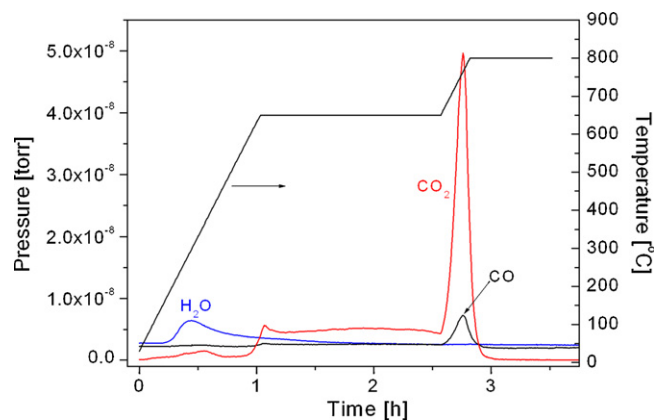
Fig. 5. Heating in He of $La_{0.7}Pr_{0.3}O_x$ (pretreated in 90% air/5% CO_2/5% H_2O, up to 650 °C), followed by cooling in He.

the oxide phase. It is therefore important to examine what the sulfidation performance would be in case the sample is solely treated at 650 °C in the air-rich mixture, where the carbonate phase is still present as dictated by equilibrium (Table 2) and additionally confirmed by the XRD patterns of Fig. 6. Sulfidation equilibria for pure lanthana and lanthanum oxycarbonate sorbents are calculated based on reactions (2) and (3) for a gas mixture composed of 50% H_2–5% CO_2–10% H_2O–He bal.

$$La_2O_{3(s)} + H_2S_{(g)} = La_2O_2S_{(s)} + H_2O_{(g)} \qquad (2)$$

$$La_2O_2CO_{3(s)} + H_2S_{(g)} = La_2O_2S_{(s)} + CO_{2(g)} + H_2O_{(g)} \qquad (3)$$

Fig. 6. XRD patterns of $La_{0.7}Pr_{0.3}O_x$; (A) as prepared, after calcination in air at 650 °C for 4 h, and (B) after pretreatment at 600 °C in 90% air–5% CO_2–5% H_2O for 30 min.

Fig. 7. Thermal decomposition of carbonate for $La_{0.7}Pr_{0.3}O_x$ calcined at 650 °C; heating rate for both steps 10 °C min^{-1}.
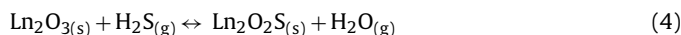
Under these conditions, both compounds can remove H_2S to ppm levels, even though the sulfidation equilibrium is more favorable for the lanthana (0.9 ppmv) than for the lanthanum oxycarbonate (7.5 ppmv).

The presence of carbonate is of concern only when the sulfidation temperature is lower than 800 °C. At this temperature, thermodynamics suggests that decomposition would occur as long as the CO_2 concentration is lower than 14%. This is the case for the sulfidation mixture of interest where only 5.6% of CO_2 is present at equilibrium. Even though thermodynamics dictate whether decomposition will occur or not, kinetics determine how fast the process will happen. It is possible to get a first measure of the carbonate decomposition kinetics by examining the thermal decomposition profiles shown in Figs. 3A and B, and 4A and B. While decomposition is very slow at 650 °C, when the temperature is ramped up to 800 °C, the evolution of CO_2 is much faster and complete decomposition is achieved. To further prove this, the sample was first heated to 650 °C in He and eventually to 800 °C always in the same gas mixture. The CO_2 concentration profile shown in Fig. 7, confirms that the decomposition starts around 600 °C, but remains incomplete even after holding the temperature at 650 °C for 1.5 h. However, as soon as the temperature is ramped up, a rather fast evolution of CO_2 is measured and complete decomposition is achieved by the time 800 °C is reached.
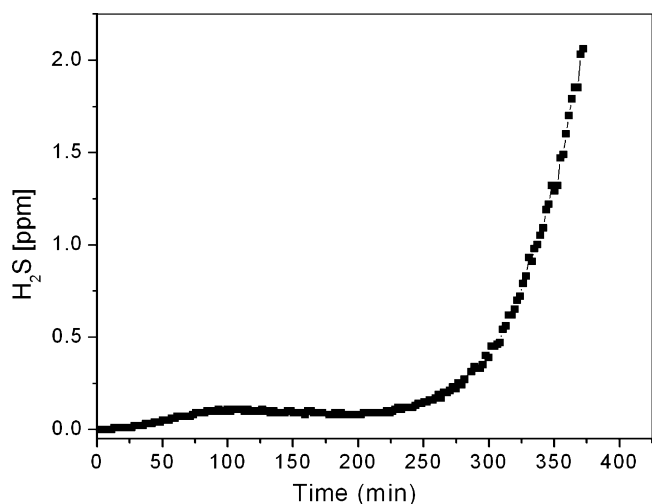
We can thus conclude that even though pretreatment in the combustor-off gas leads to sorbent carbonate formation, fast decomposition of the latter occurs when the temperature is brought up to 800 °C for the desulfurization process.

3.2. Sulfidation tests

The sulfidation performance of the samples is expressed in terms of sulfur loading, defined as mg of sulfur absorbed per gram of sorbent [mg S $g_{sorbent}^{-1}$]. The amount of sulfur absorbed by the sample is measured as the difference of the total amount flowed over the sample and the area underneath the H_2S breakthrough curve from the beginning of the sulfidation (time t_0) to the 1 ppm breakthrough (time $t_{1\,ppm}$). The theoretical sulfur loading corresponding to complete bulk sulfidation of the sesquioxides to the respective oxysulfide phases is calculated from reaction (4):
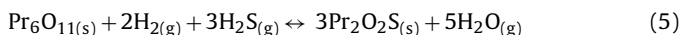
$$Ln_2O_{3(s)} + H_2S_{(g)} \leftrightarrow Ln_2O_2S_{(s)} + H_2O_{(g)} \qquad (4)$$

where Ln = La or Pr. Accordingly, 98.4 mg of S $g_{sorbent}^{-1}$ and 97.2 mg of S $g_{sorbent}^{-1}$ are the maximum attainable sulfur capacities for La_2O_3 and Pr_2O_3, respectively. It should be noted that while lanthanum has only one sesquioxide (La^{+3}), several non-stoichiometric oxides of praseodymium exist (Pr oxidation states

Fig. 8. H_2S breakthrough curve of La_2O_3 calcined at 650 °C; tested at 800 °C in 70% H_2–250 ppm H_2S–5% H_2O–He (120 mL min^{-1} and 27,000 h^{-1} S.V.); capacity at 1 ppm: 60 mg of S g$_{sorbent}$$^{-1}$.

between +3 and +4). Most praseodymium salts when calcined in air produce a tetravalent praseodymium oxide best expressed as Pr_6O_{11} [29]. In this case, sulfidation occurs according to reaction (5) and the corresponding bulk sulfur loading is 94.2 mg of S g$_{sorbent}$$^{-1}$.

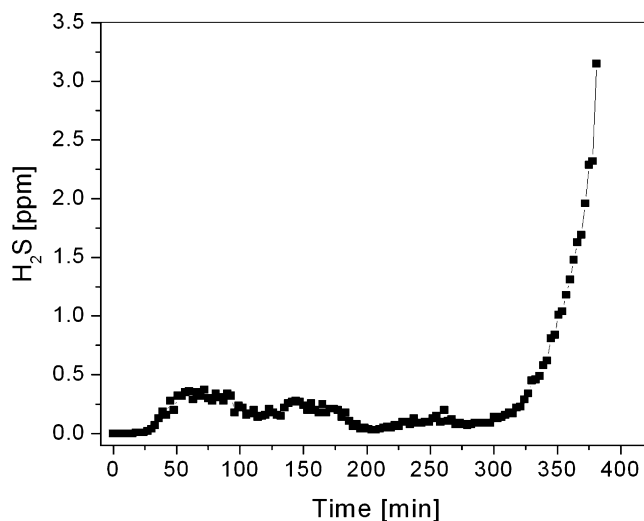$$Pr_6O_{11(s)} + 2H_{2(g)} + 3H_2S_{(g)} \leftrightarrow 3Pr_2O_2S_{(s)} + 5H_2O_{(g)} \qquad (5)$$

Thus, for any mixture of these two lanthanides the theoretical sulfur loading is expected to be in between these values depending on the atomic ratio of the two elements.

Knowledge of this ultimate sulfur capacity of the sorbent allows for an estimate of the extent of sulfidation at each set of the experimental conditions.

The sulfidation performance of the sorbents was measured while simulating the actual process conditions where the boiler off gas is used to heat up the desulfurization unit to the desired operation temperature. Hence, the samples were pretreated in a 90% air–5% CO_2–5% H_2O gas mixture at 600 °C prior to sulfidation.

Among the two test conditions examined (180,000 h^{-1} and 25,000 h^{-1}), the lower space velocity tests led to deeper bulk sulfidation of the samples as higher contact time between the gas and the solid resulted in improved diffusion. At 25,000 h^{-1} space velocity, the sulfur capacities at ∼1 ppm H_2S breakthrough were as high as 80 mg of S g$_{sorbent}$$^{-1}$ for lanthana and 50 mg of S g$_{sorbent}$$^{-1}$ for $La_{0.7}Pr_{0.3}O_x$, corresponding to 81% and 51% respectively of the maximum attainable values. The sulfur capacity of the samples at 800 °C in a gas mixture of 70% H_2–250 ppm H_2S–5% H_2O–He (120 mL min^{-1} and 27,000 h^{-1} S.V.) was also examined by monitoring the reactor outlet by GC-FPD. Over both sorbents the H_2S level was below 1 ppmv for more than 300 min, as shown in Figs. 8 and 9. The pre-breakthrough capacities at 50 ppb H_2S were 9 mg of S g$_{sorbent}$$^{-1}$ and 6 mg of S g$_{sorbent}$$^{-1}$ for the lanthana and the praseodymium-doped lanthana, respectively.

H_2S may not be the only sulfur species in the reformate gas mixture; carbonyl sulfide (COS), a product of the reactions between H_2S and CO/CO_2, can also be present in ppm amounts. Based on the gas phase equilibria and further confirmed by empty tube tests, approximately 10 ppm of COS are formed when a gas mixture of 20% H_2–25% CO–5% CO_2–5% H_2O–250 ppm H_2S is heated to 800 °C. Addition of COS into the sulfidation mixture does not shift the equilibrium since its reaction with H_2 to H_2S and CO is thermodynamically favored at the temperatures of interest. It is thus important to examine whether the sorbents exhibit good affinity


Fig. 9. H_2S breakthrough curve of $La_{0.7}Pr_{0.3}O_x$ calcined at 650 °C; tested at 800 °C in 70% H_2–250 ppm H_2S–5% H_2O–He (120 mL min^{-1} and 27,000 h^{-1} S.V.); capacity for 1 ppm: 56 mg of S g$_{sorbent}$$^{-1}$.

for COS absorption as for H_2S, as well as the effect of COS on the performance of the sorbents.

The sulfidation equilibria shown in Fig. 10 suggest that cerium, lanthanum and praseodymium sesquioxides are excellent candidates for the absorption of COS in the temperature range of 600–1200 K. To evaluate the COS and H_2S sulfur capacity of the sorbent, a supplementary experiment was carried out; the same sulfidation conditions as in Section 2.2 were used but this time 13 ppm of COS was added in the feed gas. The concentrations of COS and H_2S in the outlet gas were once again monitored by GC-FPD and their breakthrough curves are reported in Fig. 11. COS did not inhibit the absorption of H_2S. On the contrary, both gases were being absorbed simultaneously, and the breakthrough for COS followed that of H_2S. The high affinity of the sorbent for COS was also confirmed by the large sulfidation equilibrium constant (Fig. 10).

3.3. Intermittent operation

In an industrial set up unscheduled interruptions of the process might occur at any time. Of concern during intermittent operation is the stability of the partially sulfided samples; during shutdown, the
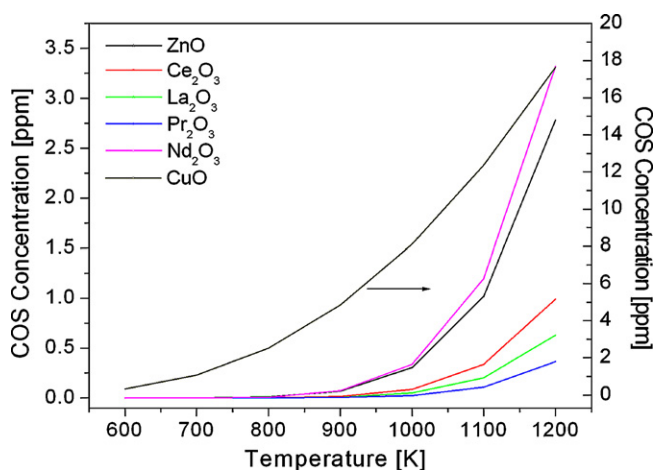
Fig. 10. Sulfidation equilibria for copper, zinc oxide and selected lanthanide oxides according to reaction $Ln_2O_{3(s)} + COS_{(g)} \leftrightarrow Ln_2O_2S_{(s)} + H_2O_{(g)}$. The sulfidation equilibrium is referring to a gas mixture containing 50% H_2–10% H_2O–10% CO–25% CO_2–He. Thermodynamic data from references [4] and [5].
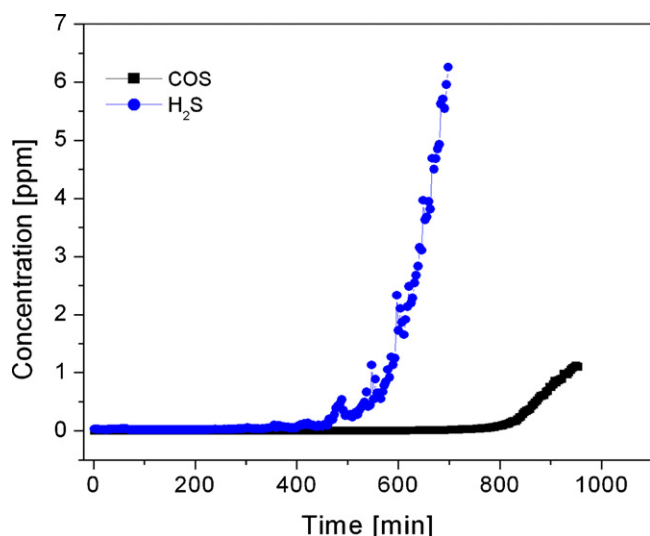
Fig. 11. H_2S and COS breakthrough curves for La_3O_2 calcined at 650 °C.

Fig. 12. H_2S breakthrough curve for $La_{0.7}Pr_{0.3}O_x$ calcined at 650 °C during simulated intermittent operation. Pretreatment and test conditions as reported in Table 4.

surface-adsorbed sulfur species on the partially sulfided material will desorb. In the start-up mode the sorbent is heated in the burner exhaust gas, containing predominantly air and some amount of water vapor and CO_2, and switching to the fuel gas stream will occur once the temperature is high enough for adsorption of H_2S to occur. It is therefore of practical interest to investigate whether the performance of the samples will be affected by such pretreatment, and to identify if H_2S/SO_2 elution is going to occur during heating up and at which temperature.

To simulate intermittent operation, sulfidation was carried out for 1 h and then the reactor was cooled down to room temperature in air. Following this, a second cycle was run. The sample was heated to the desired temperature (600 °C) in air/H_2O/CO_2. After 30 min pretreatment, the sample was heated to the test temperature (650 °C) in the same gas mixture and then the test gas mixture containing the H_2S was introduced. The details of the conditions used are shown in Table 4.

The concentration profile of H_2S during intermittent operation for the $La_{0.7}Pr_{0.3}O_x$ sample is shown in Fig. 12. It can be seen from this figure that shutting down and restarting the reactor does not modify the evolution of the breakthrough curve. In fact, the desulfurization in the second cycle picks up from where it left at the end of the first cycle and no H_2S/SO_2 elution was noticed after cooling down and reheating in air/CO_2/H_2O. However, operation of the sorbent at this low temperature lowers the sulfur capacity. Since carbonate decomposition is more favored at high temperature, it is possible that the low sulfur capacity found for the 650 °C test temperature is due to a combination of the carbonate presence and low sulfidation temperature. To further examine whether the low sulfi-
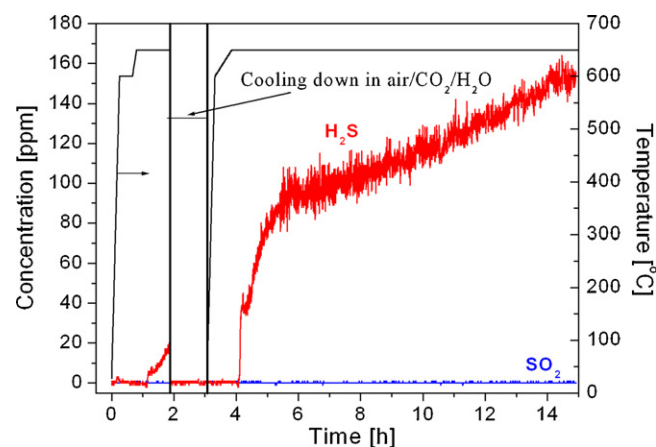
Table 4
Pretreatment and test conditions for simulated intermittent operation.

Pretreatment conditions		Sulfidation test conditions	
Temperature [°C]	600	Temperature [°C]	650
Ramping rate [°C min^{-1}]	50	Ramping rate [°C min^{-1}]	50
Space velocity [h^{-1}]	25,000	Space velocity [h^{-1}]	25,000
Flow rate [mL min^{-1}]	200	Flow rate [mL min^{-1}]	200
Duration [min]	30		
		Gas composition [mol%]	
Air	90	H_2	20
CO_2	5	CO	25
H_2O	5	H_2S [ppm]	250
		H_2O	5
		CO_2	5

dation temperature was the main reason for the low sulfur capacity found, additional tests on the fresh $La_{0.7}Pr_{0.3}O_x$ sample were carried out using the CO_2-free gas mixture, 90% H_2/He–10% H_2O to pretreat the sample at 800 °C, followed by sulfidation was at the low temperature (600 °C). The air-rich gas was also used to pretreat the sample at the same conditions. The results conclusively showed that a large fraction of the carbonate present in the sorbent was decomposed during the 800 °C-heating step. Yet, the sulfur capacity measured at 600 °C was the same whether the air- or H_2-rich pretreatment gas was used; 1.9 and 2.1 mg of $S\, g_{sorbent}^{-1}$ respectively. In other words, the overall sulfidation reaction kinetics controls the sorbent sulfur capacity.

4. Summary/conclusions

The effect of air-rich pretreatment as well as of intermittent operation on the sulfidation performance of lanthana-based sorbents was examined in the present work. These are highly efficient sulfur sorbents, and on the basis of the present findings, it can be concluded that they are stable and suitable as high-temperature filters for once-through operation. At 800 °C, the sulfur capacity at ∼1 ppmv breakthrough of H_2S exceeds $50\, mg\, S\, g_{sorbent}^{-1}$ for Pr-doped lanthana. The corresponding oxycarbonates are rapidly sulfided at this temperature.

Intermittent operation with frequent shutdowns and restarts can be handled with air-rich, boiler exhaust gas mixture. Even when the air mixture is used at a carbonate-forming temperature, such as at 650 °C, the subsequent exposure to reformate gas at 800 °C removes the carbonates. In a two-cycle sulfidation experiment, simulating intermittent operation, it was found that desulfurization in the second cycle picked up from where it left at the end of the first cycle and no SO_2 elution was noticed after cooling down and heating up in the air/CO_2/H_2O mixture in between the two cycles. Hence, these lanthanide oxide sorbents are promising candidates for highly efficient sulfur removal from hot reformate gas streams upstream of fuel cells and/or catalyst units used to upgrade the synthesis gas.

Acknowledgments

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