

Hot reformat gas desulfurization using regenerable cerium and lanthanum oxide sorbents

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Desulfurization of hot reformat gas, which is produced by catalytic partial oxidation (CPOX) or autothermal reforming of heavy fuels, such as JP-8, is required prior to using the gas in a solid oxide fuel cell (SOFC). This requires development of sorbent materials with favorable sulfidation equilibria, good kinetics, and high structural stability and regenerability at the SOFC operating temperature (650-800°C) to avoid heat exchanger penalties. Sorbent performance stability in cyclic operation of sulfidation and regeneration at such high temperatures imposes major constraints on the choice of suitable materials.

Cerium and lanthanum oxide-based materials have been developed in our lab as high-temperature regenerable sorbents for the removal of H₂S upstream of the SOFC anode.^{1,2} A major finding of our research is that H₂S can be reversibly adsorbed onto the cerium and lanthanum oxide surfaces at temperatures as high as 800 °C, on both fresh or pre-sulfided sorbents. The adsorption and desorption processes are very fast; thus, removal of H₂S to sub parts per million levels is achieved at very short (millisecond) contact times. Any type of sulfur-free gas, including water vapor, can be used to regenerate the sorbent surface. Preferably, the anode off-gas stream is used to sweep the desorbed H₂S to a burner¹.

An example is shown in Fig. 1 using fresh CeO₂ sorbent. In panel A of this figure, when He was used for regeneration, stable sulfidation/regeneration performance was reached after 10 cycles (the first seven cycles are not shown in the figure). In the first few cycles, the ratio of H₂S desorbed/ H₂S adsorbed was lower than unity due to some irreversible absorption of H₂S by the bulk sorbent material. As the bulk sorbent was gradually sulfided, the H₂S adsorption was eventually confined to the surface, reaching stable full regenerability after ten cycles. When a H₂-free water vapor stream was used as regeneration gas (panel B), some of the desorbed sulfur was oxidized to SO₂, but full regenerability was still obtained. Furthermore, when a mixture of H₂ and H₂O was used for regeneration (panel C), regenerability was still complete, but only H₂S was present in the offgas. Clearly, the choice of regeneration gas affects the chemistry: in He, some gas phase decomposition of H₂S to elemental sulfur can occur; in H₂O or O₂, production of SO₂ takes place on ceria-based sorbents,^{2,3} except at very short contact times; and finally, in the presence of H₂ only H₂S is seen. These differences do not matter if the eventual fate of H₂S is oxidation.

These results still hold, as shown in figure 2, when the sorbent was changed to pre-sulfided La_2O_3 , except no SO_2 formation was observed when the H_2 -free H_2O gas stream was used for regeneration.

It is also noteworthy that reversible adsorption/desorption was observed from the initial cycle when using pre-sulfided sorbents. This is different from what we observed in Figure 1 panel A, because H_2S re-adsorption was avoided in this test.

H_2S -TPD results¹ suggest that reversible H_2S adsorption/desorption would be possible with lanthana at temperatures lower than 500°C . This was investigated and found true for all the rare earth oxide sorbents used in our work. Results from lanthana are shown in Figures. 3 and 4. Cyclic sulfidation/regeneration tests were carried out at 400°C with the other operating conditions being kept the same as for the 800°C tests¹. As shown in Fig. 3, stabilized results were observed after the 1st cycle. The H_2S breakthrough curves in Fig. 4 display no sulfur loading degradation after 10 cycles. The stabilized sulfur loading at 1 ppm H_2S breakthrough is ~ 0.6 mg S/g_{sorbent} and $\sim 100\%$ regenerability was obtained after the first two cycles. These results further demonstrate that the operating temperature window for reversible adsorption/desorption of H_2S on lanthana is very broad; from 800°C to less than 400°C .

References

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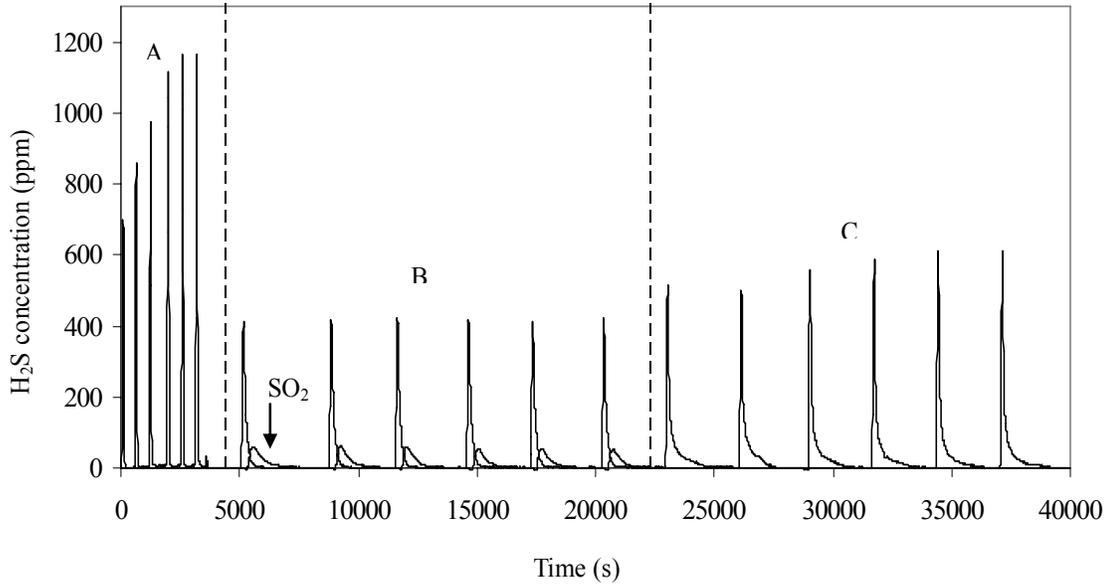


Figure 1. Cyclic sulfidation/regeneration of CeO_2 in a packed-bed reactor at 800°C using different regeneration gas compositions

Sulfidation: $0.1\%\text{H}_2\text{S}-50\%\text{H}_2-10\%\text{H}_2\text{O}-\text{He}$, S.V.= 80,000/h (STP)

Regeneration: S.V.= 80,000/h (STP); A: He; B: $10\%\text{H}_2\text{O}-\text{He}$; C: $50\%\text{H}_2-10\%\text{H}_2\text{O}-\text{He}$

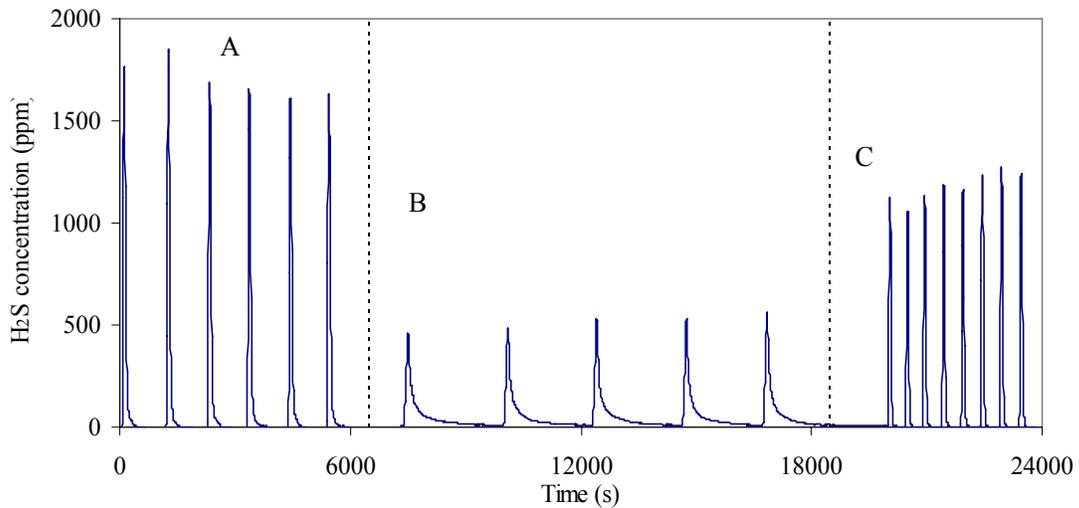


Figure 2. Cyclic sulfidation/regeneration of presulfided La_2O_3 in a packed-bed reactor at 800°C using different regeneration gas compositions

Sulfidation: $0.1\%\text{H}_2\text{S}-50\%\text{H}_2-10\%\text{H}_2\text{O}-\text{He}$, S.V.= 80,000/h (STP)

Regeneration: S.V.= 80,000/h (STP); A: He; B: $10\%\text{H}_2\text{O}-\text{He}$; C: $50\%\text{H}_2-\text{He}$

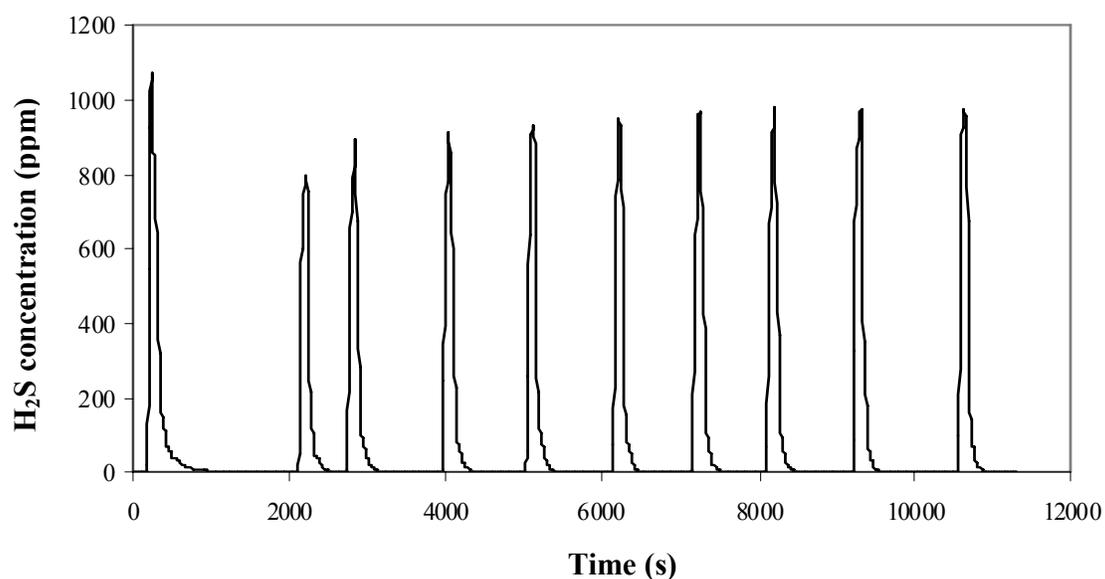


Figure 3. Cyclic sulfidation/regeneration of fresh La_2O_3 at 400°C
 Sulfidation: $0.1\%\text{H}_2\text{S}-50\%\text{H}_2-10\%\text{H}_2\text{O}-\text{He}$, S.V.= 80,000/h (STP)
 Regeneration: $50\%\text{H}_2-10\%\text{H}_2\text{O}-\text{He}$, S.V.= 80,000/h (STP)

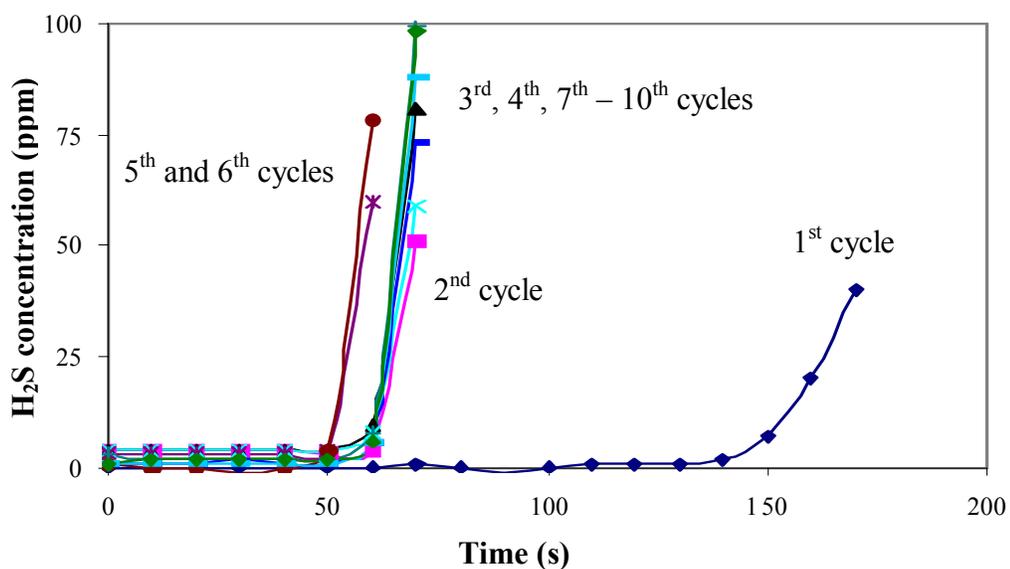


Figure 4. Cyclic H_2S breakthrough profiles from La_2O_3 at 400°C ; 1st cycle is with fresh sorbent
 Sulfidation: $0.1\%\text{H}_2\text{S}-50\%\text{H}_2-10\%\text{H}_2\text{O}-\text{He}$, S.V.= 80,000/h (STP)
 Regeneration: $50\%\text{H}_2-10\%\text{H}_2\text{O}-\text{He}$, S.V.= 80,000/h (STP)