

Cerium and lanthanum oxide-based sorbents for regenerative hot reformat gas desulfurization

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Desulfurization of the hot reformat gas produced by catalytic partial oxidation or autothermal reforming of heavy fuels, such as JP-8, is required prior to using the gas in a solid oxide fuel cell (SOFC). Development of suitable sorbent materials involves the choice of sorbents with favorable sulfidation equilibria, good kinetics, and high structural stability and regenerability at the SOFC operating temperatures (650-800°C). A major barrier is the gradual loss of sorbent performance in cyclic sulfidation and regeneration at such high temperatures.

Ce₂O₃ and La₂O₃ are excellent choices for hot gas desulfurization to < 1 ppm H₂S levels.^{1,2} Fully oxidized ceria, on the contrary, is a poor desulfurization material. The structural properties of this type sorbents in regenerative desulfurization need to be fully understood to enable proper design for the intended application. Cu-CeO_x has good sulfidation kinetics³ and was also found promising for low-temperature gas desulfurization.⁴ In recent work, we examined both La- and Cu-doped cerium oxides as high-temperature regenerable sorbents for the removal of H₂S upstream of the SOFC anode.⁵ Lanthana is a good additive, adding sulfur capacity and also thermally stabilizing ceria against sintering at high temperatures.⁶ All ceria-based sorbents were prepared by the urea coprecipitation/gelation method and calcined at 650°C in air for 4 h. This produces materials with a relatively high surface area (80-100 m²/g). However, exposure of these sorbents to the hydrogen-rich reformat gas causes sintering. Sorbent surface areas of ~ 30 m²/g were measured after 2h-exposure to the fuel gas at 800 °C. The Cu-CeO_x sorbent experienced severe sintering to < 1 m²/g after this treatment.

A major finding of our research is that all ceria and lanthana sorbents can be used regenerably, if we consider only the surface capacity of the sorbent material. In other words, we found that adsorption of H₂S on the surface of these sorbents is reversible even at temperatures >650°C.

Figure 1 shows the cyclic sulfidation/regeneration of a La-rich cerium oxide sorbent, Ce₇₀at.%LaO_x, at 650 °C and 800 °C. After the first two cycles, a sulfur loading of 3-4 mg S/g sorbent was measured at H₂S breakthrough. The much higher sulfur loading in the first two cycles was due to irreversible bulk adsorption by the lanthana portion of the sorbent. Because of the very high space velocity used in regeneration, the bulk sulfides were not regenerated.

The stabilized amount of sulfur loading in subsequent cycles is attributed to surface sulfidation only.

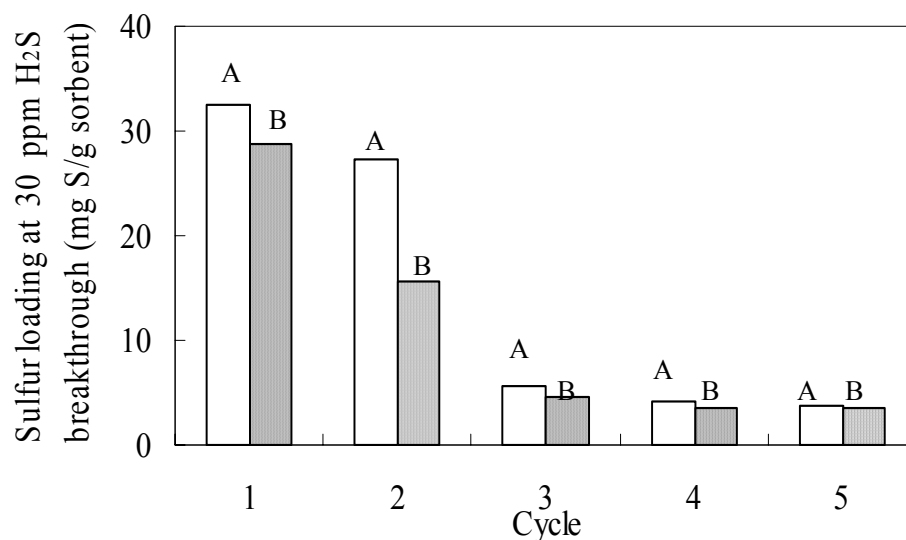


Figure 1. Sulfur capacity of Ce70%LaOx at 30ppm H₂S breakthrough in cyclic sulfidation/regeneration tests: A: Pre-reduction: 650°C, S.V.=80,000 h⁻¹; Sulfidation: 650°C, S.V.=16,000 h⁻¹; Regeneration: 650 °C, S.V.=80,000 h⁻¹ B: Pre-reduction: 800°C, S.V.=80,000 h⁻¹; Sulfidation: 800°C, S.V.=16,000 h⁻¹; Regeneration: 800 °C, S.V.=80,000 h⁻¹ Pre-reduction gas: 50%H₂-10%H₂O-He; Sulfidation gas: 0.1%H₂S-50%H₂-10%H₂O-He; Regeneration gas: 3%O₂/He.

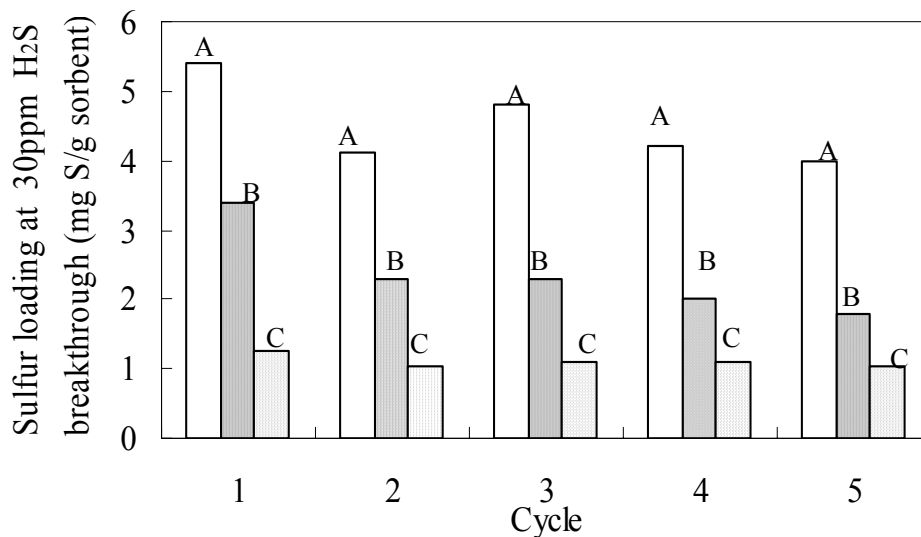


Figure 2. Sulfur capacity of 10%Cu-CeO₂ at 30ppm H₂S breakthrough in cyclic sulfidation/regeneration: A: Pre-reduction: 650°C, S.V.=80,000 h⁻¹; Sulfidation: 650°C, S.V.=16,000 h⁻¹; Regeneration: 650 °C, S.V.=80,000 h⁻¹ B: Pre-reduction: 650°C, S.V.=80,000 h⁻¹; Sulfidation: 650°C, S.V.=80,000 h⁻¹; Regeneration: 650 °C, S.V.=80,000 h⁻¹ C: Pre-reduction: 800°C, S.V.=80,000 h⁻¹; Sulfidation: 800°C, S.V.=16,000 h⁻¹; Regeneration: 800 °C, S.V.=80,000 h⁻¹ Pre-reduction gas: 50%H₂-10%H₂O-He; Sulfidation gas: 0.1%H₂S-50%H₂-10%H₂O-He; Regeneration gas: 3%O₂/He.

Figure 2 shows the cyclic sulfidation capacity of 10at%Cu-CeO₂ at 30 ppmv H₂S breakthrough. We see that this sorbent has good regenerability already from the first cycle at both temperatures, 650 °C and 800°C. At the space velocity of 16,000h⁻¹, the sulfur capacity at 650°C (~5mg S/g sorbent) is higher than that at 800°C (1-1.3 mg S/g sorbent). This can be attributed to two reasons: first, reversible sulfidation of the copper part of this sorbent takes place at 650 °C. However, the contribution of copper is lost at 800 °C due to the severe sintering of the copper and ceria particles and to the lower affinity of copper for H₂S at 800 °C. The second reason is that more extensive bulk sulfidation takes place at 650°C. This was further probed by carrying out the experiments at 650°C under higher sulfidation space velocity (80,000h⁻¹). As shown in Fig. 2, lower sulfur capacity was then measured.

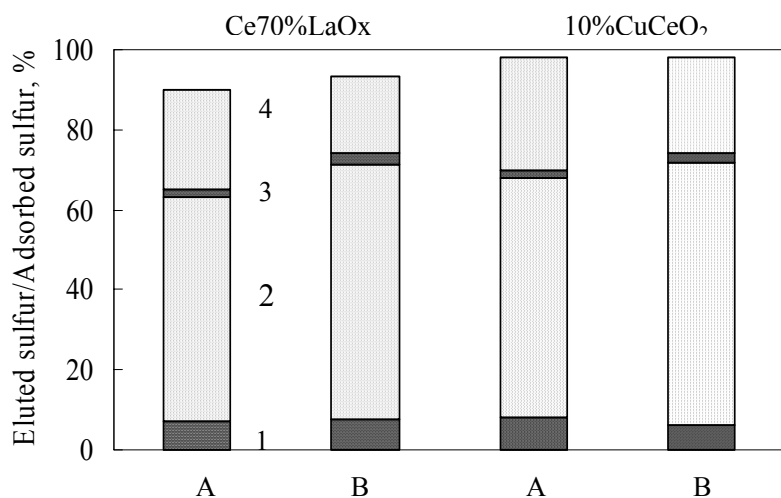


Figure 3. Stabilized regeneration offgas composition at different regeneration space velocities: A: S.V.= 80,000 h⁻¹; B: S.V. = 400,000 h⁻¹. Pre-reduction: 800°C, 50%H₂-10%H₂O/He, S.V.= 80,000 h⁻¹. Sulfidation: 800°C, 0.1%H₂S-50%H₂-10%H₂O/He; S.V. = 80,000 h⁻¹ Regeneration: 800°C, 3%O₂/He.
Legend for figure: 1: %SO₂ eluted in 3%O₂/He regeneration step. 2: %H₂S eluted in 3%O₂/He regeneration step. 3: %SO₂ eluted in 50%H₂-10%H₂O/He reduction step. 4: %H₂S eluted in 50%H₂-10%H₂O/He reduction step

We have shown that under oxidative regeneration conditions, high regeneration space velocities (> 80,000h⁻¹) can be used to suppress sulfate formation (Fig.3) and shorten the total time required for complete sorbent regeneration. This creates new opportunities for sorber/regenerator reactor designs to meet the requirements of solid oxide fuel cell systems at any scale. Alternatively, to prevent sulfate formation, other gas mixtures, such as H₂S-free reformat gas or anode exhaust gas can be used for complete regeneration. To prevent the re-adsorption or oxidation of the desorbed H₂S onto the sorbent bed, cyclic sulfidation/regeneration tests were carried out on pre-sulfided sorbents. The surface sulfur capacity of the sorbents remained unaffected.

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