

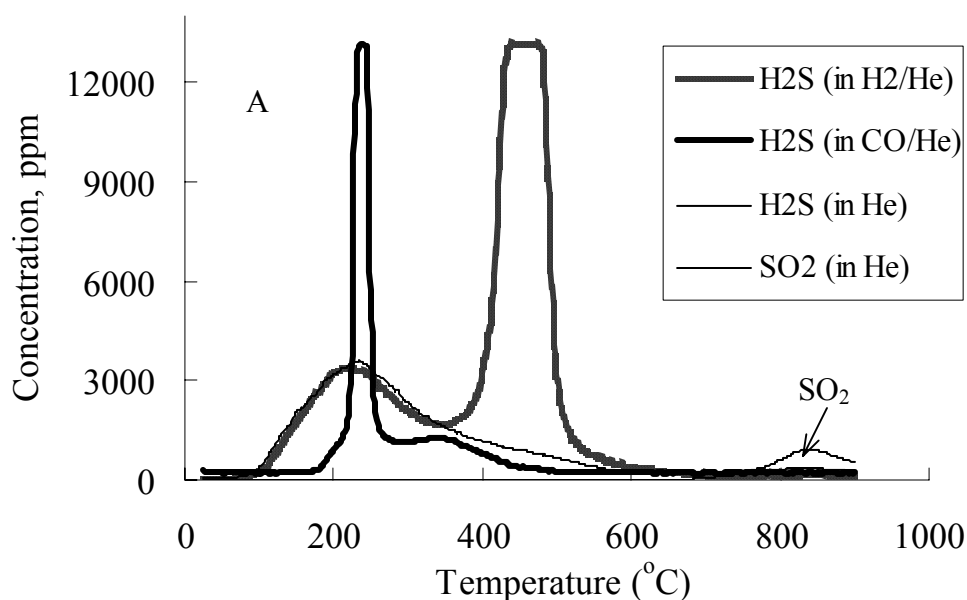
Copper and Lanthanum Doped Cerium Oxide for Hot Reformate Gas Desulfurization

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Hot reformat gas produced by reforming of heavy fuels, such as JP-8, must be desulfurized prior to its use in a solid oxide fuel cell (SOFC). This requires development of sorbent materials with high sulfur absorption efficiency and capacity 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. In on-going work in our laboratory, we have been studying mixed oxides of cerium and lanthanum or copper as high-temperature regenerable sorbents for the removal of H₂S upstream of the SOFC anode.¹ The rationale behind our choice is the excellent sulfidation equilibria of lanthana and reduced cerium oxide at these temperatures, the enhanced reducibility of ceria by the addition of lanthana and copper oxide, and the potential for recovery of sulfur in elemental form during regeneration.

All ceria-based sorbents were prepared by the urea-gelation /coprecipitation method, which gives good homogeneity and results in moderately high surface area, typically 90 m²/g after air calcination at 650 °C for 4 h.



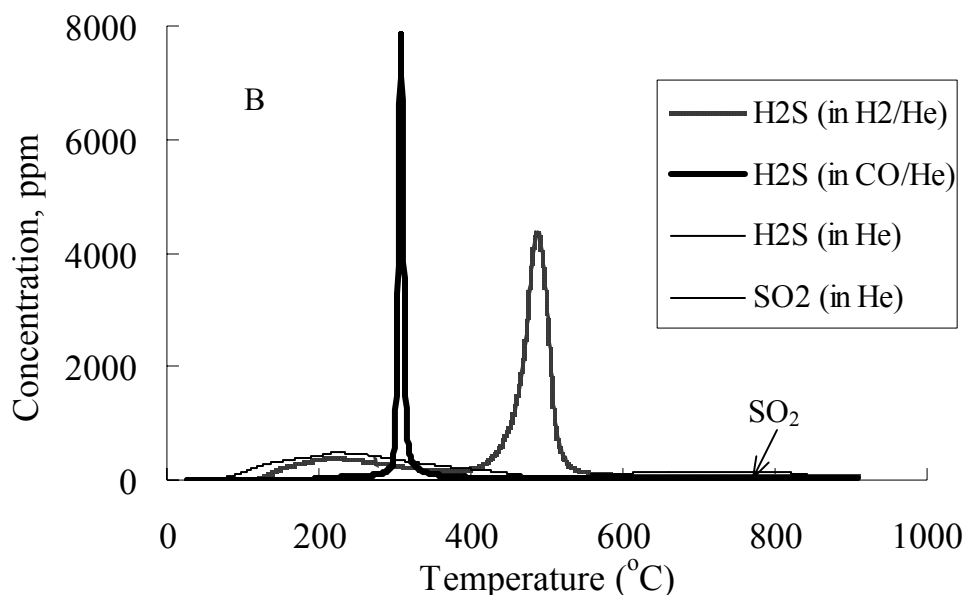


Figure 1. H₂S-TPD from Ce(30at%La)O₂ (A) and CeO₂ (B) using H₂/He, CO/He or pure He as carrier gas

By H₂S-TPD analysis of the as prepared sorbents, as shown in Figure 1, we found that the surface sulfur structures were similar on CeO₂ and Ce(30at%La)O₂, but the amount of sulfur desorbed from the latter was more than six times higher. Dissociative adsorption of H₂S was found and more than half the sulfur eluted was in elemental form.

Table 1. Surface area of fresh and pre-reduced sorbents

Sorbent	Surface area under various treatment conditions (m ² /g)		
	650 °C 4h Air	650 °C 1h 50%H ₂ -10%H ₂ O- He [#]	800 °C 1h 50%H ₂ -10%H ₂ O- He [#]
CeO ₂	84	73.1	25.1
Ce30%LaO _x	84.6	61	28.3
Ce70%LaO _x	85.3	38.2	13.8
10%Cu-CeO ₂	100	56.5	<1

[#]: Prior to this treatment, each sorbent had already been calcined at 650°C for 4 h.

To mimic the conditions in a fixed-bed sorber where most of the bed is initially exposed to sulfur-free gas, pre-reduction of the sorbents in H₂S-free fuel gas at the selected sulfidation temperature was carried out prior to each sulfidation test. The surface areas of pre-reduced samples were measured using the BET method, and results are listed in Table 1. The surface area dropped appreciably, and in the case of 10at%Cu-CeO₂ sintering was severe (surface area <1 m²/g) after the 800°C reduction. On the other hand, the lanthana-containing samples retained more than 10-60 m²/g at both reduction temperatures.

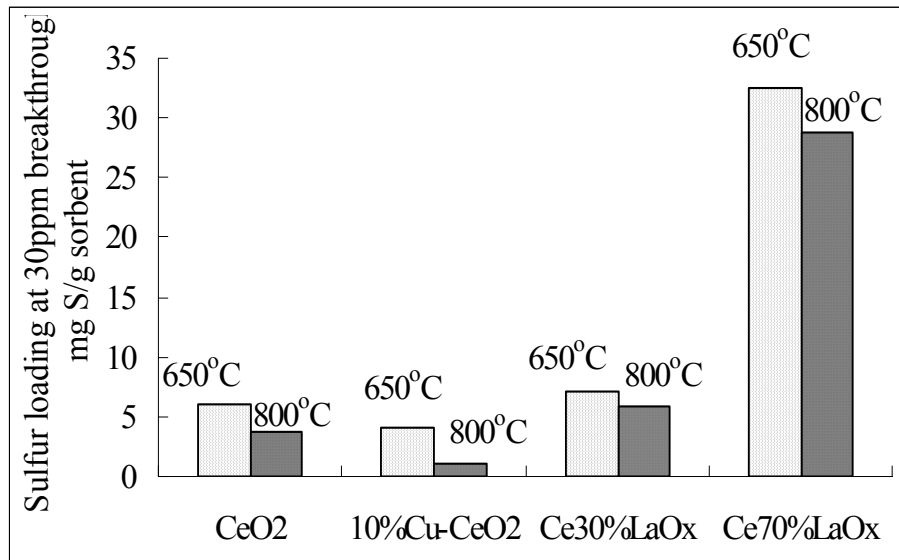


Figure 2. Sulfur loading of pre-reduced ceria-based sorbents (at 30ppm H₂S breakthrough) at different temperatures ; feed gas: 0.1% H₂S-50%H₂-10%H₂O-bal.He; S.V.=16,000h⁻¹(NTP)

Four sorbents were selected to measure the sulfidation capacity at 30ppm breakthrough after pre-reduction. From Figure 2., the highest sulfur loadings (>3 wt% at 10 ppm H₂S breakthrough levels) were measured on a sorbent containing 70 at% lanthanum under both 650 and 800°C. This high capacity is attributed to participation of lanthanum oxide in sulfidation. For each sorbent, the sulfur loading observed at 650°C is higher than that at 800°C. Combined with the results in Table 1, surface area is one of the reasons for this difference. The other, of course, is the reduced adsorption efficiency of the sorbent with temperature.

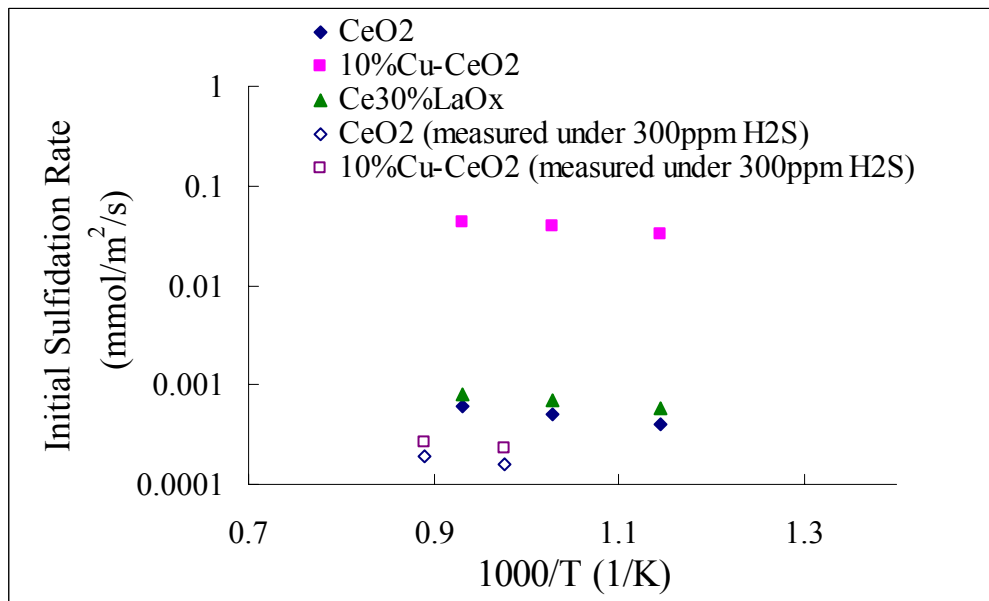


Figure 3. Arrhenius-type plot of the initial sulfidation rate of pre-reduced CeO₂-based sorbents. pre-reduction: 50%H₂-He at 800°C, 10 min; sulfidation: 0.1% or 0.03%H₂S-50%H₂-10%H₂O-He, 500 mL/min

Kinetic studies of sulfidation of pre-reduced sorbents were conducted in a thermogravimetric apparatus with a gas containing 50mol% H₂, 3% H₂O and various contents of H₂S. As shown in Figure 3, at the higher H₂S concentration (1000 ppm), the initial sulfidation rate of 10%Cu-CeO₂ is higher than that of CeO₂ and Ce30%LaO₂, while all three sorbents have similar activation energy (15±3 kJ/mol). In order to distinguish the contributions of ceria and copper to the sulfidation rate, we varied the H₂S concentration so that the sulfidation conditions were across the phase boundary between metallic copper and copper sulfide. We would then expect the copper component not to sulfide, and the sorbent to resemble the copper-free cerium oxide. Based on thermodynamic calculations,^{2,3} 300ppm H₂S was used for tests at the selected sulfidation temperatures (750 and 850°C). From Figure 3, at this H₂S concentration, the initial sulfidation rate of 10%Cu-CeO₂ is close to that of CeO₂, and on both sorbents the rates are about three times less than the sulfidation rate of CeO₂ measured with 1000ppm H₂S in the feed gas. Assuming the sulfidation reaction is first order, these results suggest that metallic copper has considerably faster sulfidation kinetics than reduced cerium oxide, while both have a similar activation energy.

Results from structural analysis of used and regenerated sorbents as well as from regeneration testing will be presented.

References

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