Hot Reformate Gas Desulfurization Using Regenerable Rare Earth Oxide Sorbents

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Introduction

Hot reformate gas produced by catalytic partial oxidation, steam or autothermal reforming of heavy fuels, such as JP-8, must be desulfurized prior to its use in a solid oxide fuel cell (SOFC). Candidate sorbent materials should have favorable sulfidation equilibria, good kinetics, and high structural stability at the SOFC operating temperature (650-800°C). A key problem with bulk oxide sorbents is their gradual loss of activity in cyclic operation due to poor regenerability and/or structural degradation as the sorbent crystal phase cycles from oxide to sulfide with sulfates also forming in oxidative regeneration [1]. The scarcity of materials that can remove H_2S to sub-ppm levels from any gas type at T > 650 °C, compounded with the poor regenerability of bulk sorbents has kept the problem of hot gas desulfurization basically unsolved, despite the attention it received over the past two decades, mostly by the DOE and its contractors in connection with the development of the IGGC process for coal plants.

We have recently reported a solution to the problem of hot gas desulfurization by using only the surface capacity of the sorbent in a process that is essentially a swing adsorption/desorption of H_2S [2].Very high space velocities can be used, making the sorber/regenerator units very small, hence suitable for compact hydrogen generators and fuel cell units. Of course, this is also a new solution for hot coal gas cleanup at a larger scale. Rare earth oxides based on lanthana are used with excellent H_2S removal efficiency and complete regenerabilty at all temperatures. In this paper we report on novel sorbent synthesis methods, the adsorption and regeneration chemistry, and sorbent characterization.

Materials and Methods

Doped and undoped cerium and lanthanum oxides and their mixtures were prepared by a variation of the urea coprecipitation /gelation method as described in [2,3]; and by a hydrolysis method aimed at preparing nanoscale rare earth oxides. Doping lanthana with Y_2O_3 increased the surface area and prevented carbonate formation. Pre-sulfided sorbents were made by sulfiding the sorbents in a gas mixture of 0.25% H_2S-50%H_2-He at 800°C. Cyclic sulfidation/regeneration experiments were run in a quartz packed-bed flow reactor. Sulfidation to 1 ppm H_2S breakthrough took place in simulated reformate gas mixtures, and was followed by regeneration until all the H_2S was desorbed. The H_2S and SO_2 concentrations in the offgas were monitored by a Western Research Series 900 UV-Visible analyzer and by a GC/FPD.

Results and Discussion

Any type of sulfur-free gas, including water vapor, can be used to regenerate the pre-sulfided lanthana surface, as shown in Fig. 1, and the performance was stable during each test. Similar results were also obtained with other pre-sulfided sorbents (CeO_2, Ce30%LaO_x).

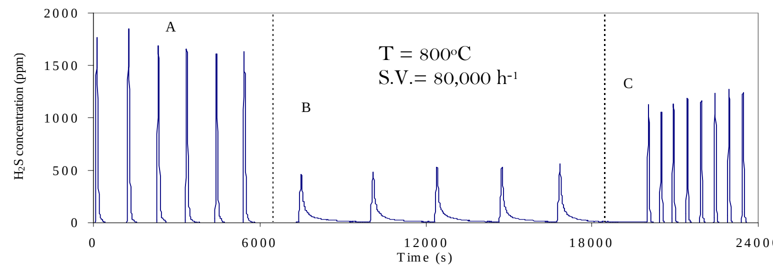

Figure 1. Cyclic adsorption/desorption of H_2S on of pre-sulfided La_2O_3. Sulfidation: 0.1%H_2S-50%H_2-10%H_2O-He; Regeneration: A: He; B: 10%H_2O-He; C: 50%H_2-He

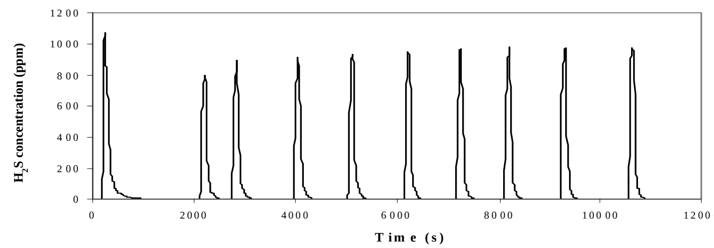

Figure 2. Cyclic sulfidation/regeneration of La_2O_3 at 400 °C
Sulfidation: 0.1%H_2S-50%H_2-10%H_2O-He, S.V.= 80,000/h (STP)
Regeneration: 50%H_2-10%H_2O-He, S.V.= 80,000/h (STP)

H_2S-TPD data shows that H_2S adsorption/desorption is possible over a wide temperature range (400-800°C), [2]. This was true for all the rare earth oxide sorbents used in our work. Results from tests carried out at 400°C on lanthana are shown in Figure 2. The surface sulfur loading at 1 ppm H_2S breakthrough was 0.6-2.5 mg S/g sorbent at all temperatures and the regenerability was 100%. Adsorption isotherms and adsorption/desorption kinetics will be presented.

Significance

Novel regenerable sorbents for hot reformate gas desulfurization have been developed. By using only the surface capacity, bulk regeneration of the sorbent with its attendant structural complexities is prevented.

References

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