Title: **HIGH EFFICIENCY DESULFURIZATION OF SYNTHESIS GAS: III**

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ABSTRACT

The high efficiency, high temperature desulfurization of synthesis gas using CeO_2 and CeO_2-ZrO_2 sorbents is being studied. In earlier research prereduced CeO_2 has been shown to be capable of reducing the H_2S content of highly reducing gases from 2500ppmv to 1ppmv or less at temperatures in the range of 650°C to 800°C. Elemental sulfur is produced directly when the sulfidation product, Ce_2O_2S, is regenerated. Twenty-five cycle tests using sulfidation and regeneration temperatures of 800°C and 600°C, respectively, show little sorbent deterioration.

The key factor in reducing the H_2S to 1ppmv or less is the ability to reduce CeO_2 to nonstoichiometric CeO_n, where $1.5 < n < 2.0$. Typical coal gas compositions, such as obtained from the Texaco and KRW processes, do not have the reducing power to form the necessary levels of CeO_n. The addition of ZrO_2 to CeO_2 in oxidation and three-way automotive exhaust catalysts is known to increase the oxygen mobility and result in increased oxygen exchange capacity. If follows, therefore, that ZrO_2 addition should also improve the performance of CeO_2 based desulfurization sorbents.

Commercially available CeO_2-ZrO_2 as well as materials prepared in-house using both electrochemical and co-precipitation methods are being characterized and tested for their desulfurization ability. The ZrO_2 content has ranged from 0% to 20% (by mol), and x-ray diffraction analysis suggests the formation of a solid solution of ZrO_2 in CeO_2. Recent attention has focused on sorbents prepared in-

house using the co-precipitation method because of the difficulty in obtaining sufficient quantities of the other materials to permit extensive desulfurization testing.

In addition to characterization by x-ray diffraction, the reducibility of the sorbents as a function of temperature and gas composition is being measured using an electrobalance reactor, and BET surface area measurements are used to correlate the experimental desulfurization results.

Desulfurization tests use a laboratory-scale, fixed-bed reactor with all parts that contact H_2S constructed of quartz, Teflon, or silcosteel to minimize interaction between H_2S and reactor surfaces. The feed gas contains H_2S, H_2, CO_2 (or H_2O) and N_2, and the proportions of H_2, CO_2, and H_2O are varied to control the gas reducing power. The H_2S concentration in the product gas is determined by gas chromatography using a pulsed flame photometric detector (PFPD) for H_2S concentrations from 0.1 to 10 ppmv and a thermal conductivity detector (TCD) for higher H_2S concentrations. Sub-ppmv H_2S concentrations have been achieved routinely during the prebreakthrough period using both CeO_2 and CeO_2-ZrO_2 sorbents, but results have not always been consistent, and we have not yet been able to confirm the advantages expected from the addition of ZrO_2.

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