Title: **High Efficiency Desulfurization of Synthesis Gas**

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Abstract

The objective of this research project is to demonstrate that ceria-zirconia high-temperature desulfurization sorbents are capable of achieving Vision 21 desulfurization goals of sub-ppmv H_2S in coal gasification process streams.

First generation zinc-based high-temperature desulfurization sorbents are not capable of the meeting the desulfurization goals of Vision 21. An alternate second generation sorbent is required to reach the sub-ppmv levels necessary to permit the desulfurized coal gas to be used in fuel cells and in synthesis gas processes. A recently completed study in this laboratory demonstrated that reduced ceria, CeO_n with $1.5 < n < 2.0$, was capable of reducing the H_2S concentration from 2500 ppmv in the inlet gas to less than 1 ppmv in the product at 700°C, a significant improvement over zinc-based sorbents at the same temperature. Other process problems associated with zinc-based sorbents were either eliminated or significantly reduced. For example, no volatile cerium compounds are formed, thereby eliminating the problem associated with the reduction of ZnO to zinc vapor. The sulfided product, Ce_2O_2S will react with SO_2 to form elemental sulfur directly during sorbent regeneration. Elemental sulfur concentrations as large as 20 mol% (based on S_2) were formed in the previous study. ZnS, in contrast, can only be regenerated using O_2 to form SO_2, and the problem of ultimate sulfur control must still be faced. Finally, sulfate formation during regeneration, which is thought to be a primary cause of zinc sorbent deterioration, is avoided with ceria since O_2 is not used during regeneration.

The factor limiting the direct application of CeO_2 is its high stability. Gas compositions from typical gasifiers such as Texaco and KRW are not sufficiently reducing to form appreciable amounts of CeO_n. The earlier LSU study used oxygen-free, high H_2 content reducing gas to form CeO_n prior to exposing the sorbent to H_2S.

Recent research involving three-way automotive and oxidation catalysts has shown that the addition of ZrO_2 to CeO_2 enhances the oxygen mobility within the crystal lattice and improves catalyst performance and thermal stability. These positive effects on catalyst redox reactions are the same factors needed to improve the performance of cerium-based sorbents in the less reducing coal gas from the Texaco and KRW processes.

Both commercially available and in-house materials synthesized electrochemically will be studied. In-house synthesis affords the flexibility of altering the structure and composition of the sorbent for optimal sulfur removal. Candidate sorbents are characterized using a variety of techniques including x-ray fluorescence, x-ray diffraction, and scanning and transmission microscopy. Electrobalance reaction tests will be used to measure the equilibrium value of n in CeO_n as a function of gas composition and temperature. Promising materials will be tested in a laboratory-scale fixed-bed reactor to determine their ability to reduce H_2S concentrations to Vision 21 levels. The reactor system will be constructed of quartz and teflon downstream of the fixed bed to eliminate interactions between low H_2S concentrations and steel surfaces. A gas chromatograph equipped with a pulsed flame photometric detector (PFPD) has been acquired to measure H_2S at sub-ppmv levels.

Journal Articles

Electrosynthesis of Nanocrystalline Ceria-Zironcia, A. Mukherjee, D. Harrison, and E. J. Podlaha, submitted.

Completed Presentations

None

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A. Mukherjee (LSU support)
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