Selective Catalysts for Hydrogen Sulfide Oxidation in Natural Gas – Concept to Commercialization.

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Introduction
In 2000, the U.S. consumed 98 quads of energy (1 quad = 10^{15} Btu) of which natural gas accounted for about 24%. Almost 25% of this gas was contaminated with H2S. In addition to being toxic and a source of polluting SO2 when flared, H2S is corrosive and therefore no more than 4 ppm H2S is allowed in pipeline gas. As a result, gas treatment to remove H2S has to be done relatively close to the well. The demand for energy is ongoing and will increase for the foreseeable future. At the same time, sulfur levels in newly-discovered fossil fuel reserves have been steadily increasing. Because SO2 is an acid rain precursor, environmental regulations will require recovery of the sulfur in these fuels, and flaring of H2S will be less and less of an option. The cost of sulfur removal from natural gas and petroleum has been estimated to be $10 billion/year. The most common method for removing H2S from natural gas is the Claus process. Multiple stages are used since the Claus reaction is limited by equilibrium, and interstage cooling, sulfur removal, and reheating are required to achieve high conversions. The Claus process is uneconomical for small plants and incompatible with gas streams containing low concentrations of H2S. Since sulfur recovery is required for many small-scale plants, operators have looked to alternate processes such as liquid redox and scavenging systems to recover the sulfur for their small-scale sour gas treating applications. Although effective, these systems have relatively high operating costs. Selective oxidation, combined with tail gas treatment offers a significant savings in both capital and operating costs over conventional treatment processes.

Results and Discussion
TDA Research, Inc. (TDA), with funding from the U.S. Department of Energy (DOE) has developed a catalytic oxidation process for sulfur recovery. The process uses a patented catalyst comprising a mixture of TiO2, Nb2O5, and MoO3 to oxidize H2S in the gas phase directly to elemental sulfur and water

\[ \text{H}_2\text{S} + \frac{1}{2} \text{O}_2 \rightarrow \text{S} + \text{H}_2\text{O} \]

(Srinivas and Bai 2000). In addition, sulfur can be recovered from very lean, noncombustible gas streams.

Figure 1 shows the various secondary reactions that can occur during the selective oxidation reaction. The H2S can undergo oxidation to SO2, the sulfur that is formed
in the catalyst bed can be further oxidized to SO$_2$ in the bed, and the sulfur formed can react with the water in the feed, or the water that is formed by the primary reaction to form H$_2$S and SO$_2$ (reverse Claus reaction). By changing the mixed metal oxide composition, temperature, and reaction conditions, we can tailor the S yield (and therefore, the SO$_2$ yield) to be between 0-100%. Lower catalyst temperatures generally favor high selectivity to S (primary reaction).

Figure 2 shows the results of a test from a statistically designed experiment. The catalyst in this run was a Fe/Mo/Nb/TiO$_2$ catalyst, tailored to obtain varying S and SO$_2$ yields with different conditions. Increasing the O$_2$/H$_2$S from 0.7 to 1.0 or increasing the temperature from 200$^\circ$C to 250$^\circ$C increases the amount of SO$_2$ formed at the expense of sulfur formation. Therefore, by adjusting the catalyst composition (changing the meta oxide component and the quantity), and the operating conditions, the SO$_2$ and sulfur yields can be controlled. The paper will discuss the effect of catalyst composition and reaction conditions on S yields, the mechanism of sulfur formation and the competing reactions shown in Figure 1 and the economics of the process. Results of an ongoing field test of the technology (pilot plant shown in Figure 3) will be discussed.

References