MECHANISTIC AND KINETIC STUDIES OF HIGH-TEMPERATURE COAL GAS
DESULFURIZATION SORBENTS

Susan Lew
Maria Flytzani-Stephanopoulos
Adel F. Sarofim

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by
Massachusetts Institute of Technology
Department of Chemical Engineering
Cambridge, Massachusetts

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Progress Summary

During this quarter work on the reduction of zinc titanate materials was written-up as a journal article and submitted for publication. The manuscript of this paper, entitled "The Reduction of Zinc Titanate and Zinc Oxide Solids", is hereby submitted to the DOE as part of our quarterly report.

On the basis of the completed parametric studies of reduction and sulfidation (effects of H_2 , H_2O , see quarterly reports #7, 8), ZnO and Zn-Ti-O materials were evaluated in terms of reduction-sulfidation kinetic differences. Comparative Arrhenius plots of the initial reduction and sulfidation rates are shown in Figure 1 for the sorbents ZnO, Z2T-a ($2Zn:1Ti$) and Z2T3-a ($2Zn:3Ti$). The reduction rate is shown for a gas containing (mol) 10% H_2 -3% H_2O -87% N_2 , while sulfidation is for 2% H_2S -98% N_2 . The point at which the initial reduction rate becomes faster than sulfidation rate is 848, 872 and 942°C, respectively, for ZnO, Z2T-a and Z2T3-a. Therefore, Zn-Ti-O solids can be used for the desulfurization of coal-derived fuel gas at higher temperatures than single ZnO. For sorbent Z2T3-a, the desulfurization temperature can be 94 degrees Celcius higher than for ZnO. Moreover, as reported in the previous quarterly report (DOE/PC/88927-8) the presence of TiO_2 largely suppresses the gross morphological effects observed on ZnO particles as a result of sulfidation in the presence of high hydrogen concentrations. The appearance of macroscopic cracks and the formation of fine particles of ZnS by the elution and reaction, respectively, of zinc vapor, $Zn(g)$, with $H_2S(g)$ limit the application of single ZnO to lower H_2 -containing gas streams and lower temperatures. Another issue is the loss of surface area (sintering) by H_2O . While this was similar for both ZnO and Zn-Ti-O materials, (see Report #DCE/PC/88927-7), it is alleviated for zinc titanates by the redispersion (surface area increase) observed upon sulfidation of these sorbents.

These observations offer interesting possibilities for reactor design. Desulfurization in a fixed-bed reactor will lead to zinc loss. Because of the gradient in H_2S concentration as a function of sorbent bed axial position, a portion of the sorbent bed will be in contact with a H_2S -free reducing gas. In this part of the bed, zinc loss can occur. On the other hand, desulfurization in a fluidized bed reactor offers the possibility of eliminating zinc loss. The disadvantages of this reactor configuration, however, are lower H_2S removal efficiency (due to bubbling) as well as the fact that the vapor phase reaction between H_2S and Zn will produce fines and will lead to sorbent elutriation and loss. For the fluidized bed reactor, mixed Zn-Ti oxides would still be preferable as sulfur sorbents over ZnO because of lower particle disintegration (due to crack formation) and fines production.

Regeneration of Bulk Zn-Ti-O Sorbents In order for Zn-Ti-O solids to be used commercially for the desulfurization of hot fuel gases, the sulfided solids must be regenerable. To determine the regenerability of Zn-Ti-O solids and their sulfidation performance after regeneration, two cycles of consecutive sulfidation-regeneration were performed with ZnO and Z2T-a. The results are shown in Figure 2 in terms of the dimensionless weight W/W_o (where W is the instantaneous and W_o is the initial weight of the solid) versus the reaction time. Prior to the first cycle, the solids were reduced in 10% H_2 -90% N_2 for seven minutes. The partially reduced solids were then sulfided in 2% H_2S -

98% N₂. After sulfidation, regeneration was performed in air (21% O₂-79% N₂). All reactions were performed at 650°C. The more rapid decrease in sulfidation rate of sorbent Z2T-a, seen in Figure 2b, is attributed to the presence of non-uniform grain size distribution in the solid. In the first cycle, regeneration of Z2T-a and ZnO was essentially complete after 40-50 minutes. Based on the final weight after regeneration, little if any zinc sulfate (ZnSO₄) was formed during regeneration. In the second cycle, the sulfidation performance of ZnO became worse when compared with the first cycle. As shown in Figure 2a, the sulfidation rate in cycle 2 decreased noticeably after approximately 90% conversion (W/W₀=1.06). In contrast, the sulfidation of Z2T-a (Figure 2b) in cycle 2 was the same as in the first cycle. In the second regeneration, the performance of both Z2T-a and ZnO became slightly worse. After 40-50 min, regeneration of both Z2T-a and ZnO was about 95% complete.

Work Forecast for Next Quarter

A journal article on "the Sulfidation of Zinc Titanate and Zinc Oxide Solids" will be written and submitted for publication. Work on the modeling of Zn-Ti-O sulfidation will be completed.

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COMPARISON OF INITIAL SULFIDATION AND REDUCTION RATE

Figure 1

Figure 2 Sulfidation-regeneration cycles of a) ZnO and b) Z2T-a.
1. Reduction in 10% H_2 -90% N_2 ; 2. Sulfidation in 2%
 H_2S -98% N_2 ; 3. Regeneration in 21% O_2 -79% N_2 .

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