HIGH-TEMPERATURE REGENERATIVE REMOVAL OF H_2S BY POROUS MIXED OXIDE SORBENTS

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ABSTRACT

Several mixed-metal oxides ($ZnFe_2O_4$, $CuFe_2O_4$, $CuAl_2O_4$, Cu-Fe-Al-O) were investigated as regenerable sorbents for the high-temperature removal of H_2S. A special technique was used to prepare the sorbents in a highly porous form. The sorbents were subjected to successive sulfidation/regeneration cycles in a packed bed microreactor. Sulfidation was carried out at 538-650°C with H_2S-H_2O-H_2-N_2 mixtures, regeneration with O_2-N_2-H_2O mixtures. The fresh, sulfided and regenerated sorbents were analyzed by XRD. Solid conversion and pre-breakthrough exit H_2S concentration are discussed in terms of physical structure and thermodynamic properties of the sorbents. In the case of $CuFe_2O_4$, $CuAl_2O_4$ and $CuFeAlO_x$, sorbent performance is discussed in terms of changes in the oxidation states of copper and iron during sulfidation.

INTRODUCTION

High temperature desulfurization of coal-derived fuel gas offers potential improvements on the thermal efficiency of systems using coal gasification such as power plants (high temperature fuel cells, combined cycle) and synthesis gas conversion plants (ammonia, methanol). Over the last ten years, several sorbents have been proposed and investigated for the regenerative removal of the main sulfur compound, i.e. hydrogen sulfide, from fuel gas at high temperatures. The level of H_2S removal needed depends on the end use of the fuel gas. For power plant combustion purposes, removal down to about 100 ppm is adequate, but for molten carbonate fuel cell applications removal down to a level of 1 ppm may be required.

The thermodynamics of various sorbents have been analyzed in (1) and (2) among other reports. Comprehensive surveys of experimental work encompassing various high temperature sorbents have also been published (1-7).

The overall performance of a sorbent depends on a variety of properties. Thermodynamics and kinetics of sulfidation are obvious factors, for they determine the overall sulfur capacity before breakthrough of some predetermined level of H_2S. Kinetics encompasses the rates of purely chemical steps as well as the rate of pore diffusion and, more crucially, diffusion in the sulfide product layer. Surface area and pore size distribution are very important sorbent properties as they determine the rate of these diffusional processes. Zinc oxide, one of the most promising and widely studied sorbents, has very high equilibrium constant for sulfidation but in its unsupported form suffers from slow kinetics limiting its sulfidation capacity. Iron oxide, on the other hand, has rapid kinetics but its equilibrium constant for sulfidation is not adequate for the degree of H_2S removal required in the molten carbonate fuel cell application.

The other important sorbent properties refer to stability or regenerability in extended use, the operating conditions required for regeneration, and the composition of the regeneration off-gas, which largely determines the choice of a downstream sulfur recovery process. Using zinc oxide as an example again, it is well known that evaporative loss of metallic zinc places an upper limit on the sulfidation temperature. Loss of surface area during regeneration places an upper limit on the temperature or necessitates a more complicated regenerative treatment. The regeneration off-gas including sulfur dioxide, hydrogen sulfide and elemental sulfur requires further treatment for sulfur recovery. When the yield of elemental sulfur

is sufficiently high, sulfur recovery can be simplified with significant overall cost benefits (6).

With several of the thermodynamically favorable H_2S sorbents reported to date, slow rates of reaction and pore diffusion, sintering, and pore plugging limit sorbent capacity and degree of purification under practical conditions. Such is the case with some commercial ZnO sorbents where reported conversions at breakthrough were less than 20 percent.

Recent research has shifted from pure to mixed metal oxides with the goal of improving sorbent performance. For example, zinc ferrite has been found to possess better capacity and regenerability than pure zinc oxide (5). Mixed ZnO-CuO has been studied for its better resistance to surface area loss (8) and various other mixtures including $ZnO-Cr_2O_3$ and $ZnO-Al_2O_3$ have been studied with the objective of increasing the yield of elemental sulfur during regeneration (6). Mixed oxides form various distinct crystalline phases or solid compounds, and should generally possess different thermodynamic properties and reactivity with respect to reduction, sulfidation, and regeneration reactions. This has so far received limited attention.

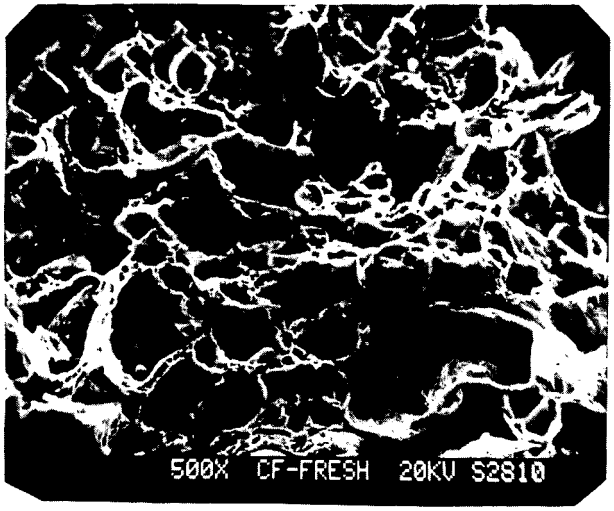
The preceding discussion emphasizes the variety of properties impacting sorbent performance and points out the need for synthesis of sorbents combining several desirable properties. On-going research at the Jet Propulsion Laboratory aims at developing improved sorbents for desulfurization of hot coal-derived gas streams. Two classes or sorbents have been developed (9,10) both characterized by rapid kinetics of absorption and good sorbent regenerability during operation at 500-700°C. Detailed description of the first class of sorbents, which consist of supported mixed oxides that form eutectic melts coating the pores of high surface area supports at the operating temperatures, can be found in recent reports (9,10). In this paper, we limit our discussion to the second class of sorbents investigated in our work. This consists of unsupported mixed oxides forming highly dispersed solid solutions or solid compounds characterized by small crystallite size, high porosity and relatively high surface areas. The sorbent is a mixture of Cu or Zn oxides with one or both of Al and Fe oxides prepared in a special manner which provides the sorbent in a highly porous form with a range of pore sizes. This prevents fouling of the sorbent during absorption and/or regeneration cycles.

EXPERIMENTAL

a) Sorbent Preparation

Several methods are described in the literature (11-14) for synthesizing highly dispersed mixed oxides. Early attempts to form high surface area metal oxide sorbents by precipitating mixed carbonates from homogenous salt solutions followed by drying and calcining resulted in materials of low surface area, about 5-8m^2/g. The bulk sorbents either in single or mixed form were then prepared by a technique that resulted in high pore volume and surface area. Following a general procedure suggested in the literature (14), an aqueous solution of thermally decomposable metal salts in the desired proportion and an organic polyfunctional acid containing at least one hydroxy - and at least one carboxylic function is rapidly dehydrated under vacuum at a temperature of 70°C. An amorphous solid foam forms which is calcined at an elevated temperature above 300°C, usually 500°C to 600°C, to form a mixed oxide phase. The crystallized mixed oxides thus formed are homogenous and highly porous.

This method was used to prepare the bulk sorbens CF ($CuFe_2O_4$) ZF ($ZnFe_2O_4$), CA ($CuAl_2O_4$), CFA ($2CuO\ Fe_2O_3\ Al_2O_3$), and others. All these materials were prepared as dispersed microcrystalline solids with high porosity. To illustrate the porous structure of these solids, scanning electron micrographs (SEM) of copper ferrite ($CuFe_2O_4$), before and after sulfidation, are depicted in Figure 1. The micrographs show very large ($\geq 10\mu m$) as well as submicron size pores. The gross porous structure before and after sulfidation, appears very similar. X-ray diffraction analysis (XRD) using Cu Kα source on a Siemens Allis D 500 instrument showed that the mixed oxides $ZnO-Fe_2O_3$ and $CuO-Fe_2O_3$ had the ferrite-spinel structure, $ZnFe_2O_4$ and $CuFe_2O_4$, respectively, while $CuO-Al_2O_3$ formed the aluminate spinel $CuAl_2O_4$. The CFA sorbent had



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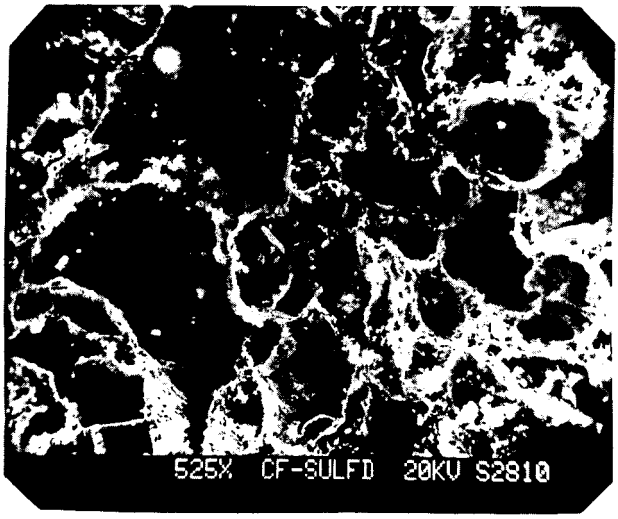

Figure 1. Scanning Electron Micrographs of Fresh and Sulfided Copper Ferrite.

a surface area of 26 m^2/g and consisted of crystalline CuO, $FeAl_2O_4$, $CuFe_2O_4$, and amorphous Al_2O_3 phases. Low angle XRD analysis of $ZnFe_2O_4$ revealed a microcrystalline structure with average crystallite size of 890Å.

b) Reactor System and Experimental Procedures

The experiments were performed in a quartz microreactor, 1 cm I.D. x 41 cm length, mounted vertically inside an electric furnace and instrumented with a K-type thermocouple moving inside a quartz thermowell (0.3 cm I.D.) concentric to the reactor. The sorbents were loaded in the microreactor as -20+40 mesh particles. The unsupported sorbents were mixed with low surface area zirconia or alumina particles, which served as an inert filler. The use of the inert particles allows to compress the experimental run time by decreasing the bed capacity, while maintaining the same space velocity. Different gases from cylinders passed through purifiers and then through calibrated flowmeters into a common gas line. The gas mixture then passed through the reactor in the upward or downward direction. The lines leading to the reactor were heated and insulated. Nitrogen bubbling through water maintained at constant temperature in a 3-neck flask assembly was used to introduce known amounts of water vapor into the feed gas stream. Temperatures at various locations in the reactor system were monitored by K-type thermocouples connected to a multi-channel digital readout. The reactor pressure in all cases was slightly above atmospheric.

The experiments consisted of consecutive sulfidation and regeneration runs. In a sulfidation run, the sulfur-free sorbent was exposed to a feed gas containing H_2(15-30%), H_2O(7-25%), H_2S(0.2-1%) and N_2 (balance). The temperature was in the range of 500-700°C and was held fixed for the duration of sulfidation. Sulfided sorbents were regenerated using a nitrogen-air or steam-air mixture at temperatures of 600-750°C. The product gas was passed through ice traps to condense any elemental sulfur formed and was analyzed for H_2S and SO_2 by a gas chromatograph HP-5830A equipped with a flame photometric detector. An absorber loop containing iodine solution, installed in the exit line from the gas-sampling valve, was used for the analysis of the total sulfur gases (H_2S, SO_2) produced during regeneration. The amount of sulfur gases absorbed was determined by titrating the excess iodine with a sodium thiosulfate solution. Elemental sulfur collected in the traps was dissolved in a sodium sulfite solution and analyzed by a standard iodometric titration method.

EXPERIMENTAL RESULTS AND DISCUSSION

The results presented in this section concern the concentration of hydrogen sulfide in the product gas during sorbent sulfidation. In a typical experiment this concentration rises very slowly at first until a certain time after which it rises rapidly to the inlet value. The time of this abrupt change of slope is called the breakthrough time, and the whole concentration vs. time curve is sometimes called a breakthrough curve. In the absence of transport and kinetic limitations the breakthrough curve would be the step function, $y=y^e$ at $t<t^*$, $y=y^o$ at $t>t^*$, where y^e, y^o are the equilibrium and inlet mole fractions of hydrogen sulfide, and t^* is the theoretical breakthrough time, i.e., the time required for complete sulfidation of the sorbent. Finite reaction and diffusion rates, axial dispersion and channeling produce experimental breakthrough curves that are smoothly sloping. The fractional conversion at the actual breakthrough time provides a measure of sorbent utilization efficiency, while the level of H_2S before breakthrough is also an important measure of sorbent performance.

The results below are presented and discussed in terms of the mole fraction of H_2S in the product gas versus the normalized time t/t^* (sorbent conversion).

$ZnFe_2O_4$ Sorbents

Zinc ferrite is one of the most efficient H_2S sorbents. Extensive lab-and/bench-scale tests with $ZnFe_2O_4$ have been performed at DOE/METC (5). The material used in that work was prepared by United Catalysts, Inc., by the conventional technique of high-temperature (>800°C) heating of mixtures of the pure oxide powders.

The surface area of this zinc ferrite, designated METC-ZF, is ~5 m^2/g and its pore volume ~0.3 cc/g.

The performance of porous zinc ferrite (ZF) synthesized in this work with high surface area and large pore size was tested in the quartz microreactor and compared to the METC-ZF sorbent at the same operating conditions. Both sorbents were used as -20 +40 mesh particles mixed with low surface area alumina particles.

At 538°C (1000°F) sulfidation temperature, the stable pre-breakthrough conversion of ZF sorbent was >0.75, while that of METC-ZF was 0.35-0.40. Both sorbents were capable of removing H_2S from ~2500 ppm to less than 1 ppm level with a feed gas containing 20 vol% H_2 and 6.5 vol% H_2O. The higher conversion of ZF must be attributed to its different physical properties. SEM micrographs of the sulfided ZF and METC-ZF sorbents show that the pore structure of the two is very different, with METC-ZF lacking the large pores of ZF. The gross morphological features of the latter were the same before and after sulfidation which is indicative of high accessibility to H_2S and limited or no pore mouth blocking.

Similarly high conversion (>0.75) was obtained with ZF at all temperatures 538-650°C and with a sulfidation gas containing 15-20% H_2, 7-25% H_2O, 0.21% H_2S, balance N_2 by volume. Figure 2 shows H_2S breakthrough curves with the ZF sorbent at 600°C sulfidation/regeneration. Very sharp elution profiles, indicative of fast reaction and diffusion rates, are observed in this figure. A limitation of all zinc ferrite sorbents, however, is that at sulfidation temperatures $\geq$600°C, zinc metal loss takes place (via reduction of ZnO). In deposits collected from the cooler part of the reactor tube, zinc has been identified by Atomic Absorption (AA) analysis. Loss of zinc could not be prevented even with high H_2O and low H_2 concentrations in the feed gas. At 600°C, at the conditions of Figure 2, the rate of evaporative Zn loss was 8 and 26 weight percent per 1000 hours at space velocities of 2100 and 6900 hr^{-1}, respectively. The corresponding content of Zn vapor in the gas phase was ~1.3 ppm, close to the equilibrium value for the ZnO reduction. Therefore, under typical sulfidation conditions, ZnO reduction will rapidly reach equilibrium. A slow decline in conversion, observed between the first and fourth cycles of sulfidation / regeneration in Figure 2, may be attributed to zinc metal loss.

$CuFe_2O_4$ Sorbents

Bulk porous copper ferrite was investigated with the hope of avoiding two difficulties that arise with zinc-based sorbents, namely the loss of metallic zinc at temperatures $\geq$600°C and the high ($\geq$700°C) regeneration temperatures required for decomposition of zinc sulfate.

Copper oxide by itself is known to reduce to the metal under the conditions of temperature and feed composition employed. Metallic copper, in turn, is sulfided according to the reaction

$$2\ Cu + H_2S = Cu_2S + H_2 \qquad 1)$$

For a feed gas with 20 mol% H_2, the equilibrium H_2S level is 44.5 ppm at 538°C and 89 ppm at 650°C. Although these levels are quite high it was thought that the equilibrium with copper ferrite could be lower because of its different crystal structure.

The copper ferrite (CF) sorbent was prepared by the technique described earlier. H_2S breakthrough curves in several sulfidation cycles at 538°C showed that the pre-breakthrough sorbent conversion was high (~0.80) and stable (over 6 cycles), Figure 3. In all cases the pre-breakthrough H_2S level was below the value of 44.5 ppm calculated for the equilibrium of reaction 1. In fact, the H_2S level remained below 2 ppm until 0.5 conversion and then gradually increased to <10 ppm when the conversion reached 0.78.

In two sulfidation/regeneration cycles carried out at 600°C, sub-equilibrium H_2S levels were again measured till breakthrough, which occurred at ~0.80 sorbent conversion. At 650°C sulfidation temperature, however, while a similarly high and stable sorbent conversion took place, the pre-breakthrough H_2S level at 0.80

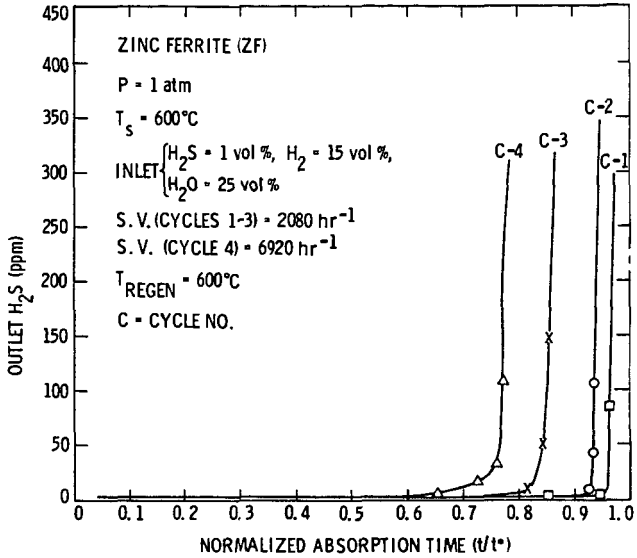

Figure 2. Breakthrough Curves in Successive Sulfidation Cycles of ZF Sorbent ($ZnFe_2O_4$) at 600°C.

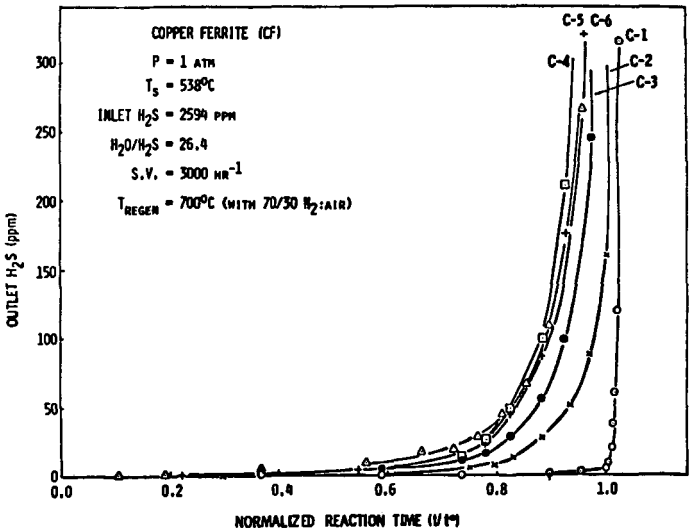

Figure 3. Breakthrough Curves in Successive Sulfidation Cycles of Copper Ferrite.

sorbent conversion was 85-90 ppm, close to the equilibrium for reaction 1. Up to 0.20 sorbent conversion, sub-equilibrium H_2S levels were measured, perhaps indicative of chemisorption effects.

Characterization of fresh, sulfided and regenerated samples of CF-sorbents was performed by SEM and XRD analyses. As shown in Figure 1, the gross porous structure of the sorbent before and after sulfidation appeared very similar in SEM (as in the case of zinc ferrite). XRD analysis of the sorbent sulfided at 538°C identified the mixed sulfide compound $CuFeS_2$ (chalcopyrite) along with $Fe_{1-x}S$, Fe_3O_4, unconverted $CuFe_2O_4$ and some amorphous material. In the sample sulfided at 650°C, the phase $CuFeS_2$ was absent, while there was indication of a poorly crystalline Cu_2S phase.

These results suggest that at 538-600°C sulfidation temperatures, CuO is stabilized towards reduction in the ferrite-spinel. The presence of $CuFeS_2$ in the sample sulfided at 538°C along with the observed pre-breakthrough H_2S levels correspond to the sulfidation reaction:

$$CuFeO_2 + H_2S = CuFeS_2 + H_2O \qquad 2)$$

The intermediate compound $CuFeO_2$ indicates a step-wise reduction of $CuFe_2O_4$. The equilibrium H_2S levels for reaction 2 were calculated by using thermodynamic values for the compound $Cu_2O \cdot Fe_2O_3$ (15). These are in agreement with the experimental H_2S levels, and much below the values for metallic copper sulfidation, reaction 1. At the higher sulfidation temperature of 650°C, reduction to metallic copper is very fast, and controls the pre-breakthrough levels of H_2S after an initial sorbent conversion of 0.15-0.20 at sub-equilibrium H_2S exit levels.

$CuAl_2O_4$ Sorbents

The stability of porous copper aluminate (CA) of the spinel crystal structure was investigated in a series of sulfidation/regeneration tests at 538-650°C. The results were very similar to copper ferrite. Thus, at 538-600°C, the H_2S pre-breakthrough levels were below the equilibrium for reaction 1, and high (>0.75, based on Cu_2S) and stable (over 5-6 cycles) sorbent conversion was observed. Copper in the +2 or +1 oxidation state was apparently stabilized in the alumina matrix and controlled the exit level of H_2S till breakthrough. At 650°C, the H_2S exit levels after ~0.20 sorbent conversion corresponded to sulfidation of metallic copper. With copper aluminate, however, structural changes that occurred at 650°C were reversed when the temperature was lowered to 538°C. This was not true with copper ferrite sorbents.

Mixed Cu-Fe-Al-O (CFA) Sorbents

In view of the enhanced stabilization of copper oxide in copper aluminate sorbents, a mixed copper ferrite-copper aluminate material, CFA, with $2CuO:Fe_2O_3:Al_2O_3$ molar ratio was prepared in porous bulk form (with 26 m^2/g surface area) as a potential sorbent for higher (>600°C) temperature H_2S removal. Under similar operating conditions, this sorbent was superior to either copper ferrite or copper aluminate in regard to pre-breakthrough H_2S levels, which were lower than the equilibrium of reaction 1 at all temperatures, 538-650°C. An example is shown in Figure 4 for 650°C sulfidation temperature with a gas containing 20 vol% H_2, 25 vol% H_2O, 1 vol% H_2S, balance N_2. The performance was stable over five cycles of sulfidation/regeneration with a high pre-breakthrough sorbent conversion of 0.75. In addition, remarkably high H_2S removal efficiency was achieved by this sorbent, with pre-breakthrough H_2S levels in the range of 0-10 ppm up to 0.50 sorbent conversion and less than 35-40 ppm at breakthrough. These levels are well below the corresponding equilibrium (89 ppm) for metallic copper sulfidation at 650°C.

XRD analysis of the fresh and sulfided (after cycle 4) CFA sorbent was performed to identify stable crystalline phases that may be responsible for the improved performance of this sorbent. The fresh CFA consisted of $CuFe_2O_4$, CuO, $FeAl_2O_4$ and some amorphous material (probably Al_2O_3), with $FeAl_2O_4$ (iron aluminate) in highly-

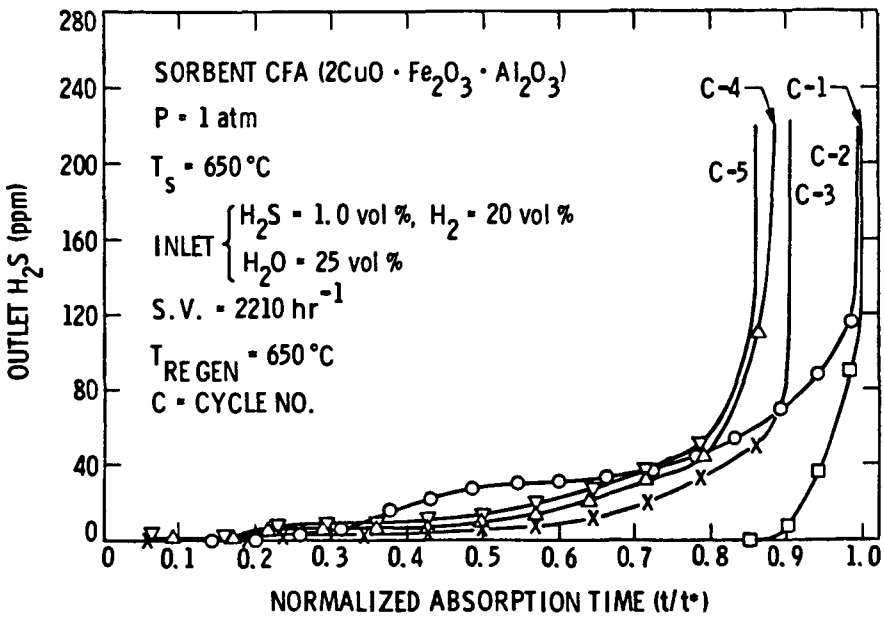

Figure 4. Breakthrough Curves in Successive Sulfidation Cycles of Sorbent CFA at 650°C.

microcrystalline form. The sulfided sample contained CuS, FeS and $CuFe_2S_3$ along with amorphous (to XRD) alumina. These results are very important, indicative of stabilization of both Cu^{2+} and Fe^{2+} in the sorbent matrix and associated improved absorption equilibria.

Additional testing of the stability and performance of the CFA sorbent was conducted with a coal gasifier gas simulant containing 17% H_2, 12% CO, 10%CO_2, 24% H_2O, 0.5-1% H_2S, balance N_2 by volume. Similar results to those shown in Figure 4 were obtained. Different conditions used in regeneration did not affect the performance of the sorbent. Other parametric studies with CFA included testing at a lower (~1000 hr^{-1}) space velocity, and different H_2S concentrations in the sulfidation gas. No significant effect on the sorbent performance was observed. A total of fourteen cycles of sulfidation/regeneration were run with CFA at 650°C. The surface area of the sulfided sorbent at the end of the fourteenth cycle was ~$8m^2/g$, still a moderately high value, especially after the frequent and extended use of CFA at 700°C (during regeneration).

Another series of tests with a different batch of CFA sorbent were conducted at the higher temperature of 830°C with a reactant mixture containing 30 mol% H_2, 17 mol% H_2O, 1 mol% H_2S, balance N_2, simulating the Texaco gasifier-fuel gas. In three cycles, breakthrough of H_2S took place at complete (100%) sorbent conversion, while the pre-breakthrough H_2S level was zero up to ~0.20 sorbent conversion and 250-270 ppm until final breakthrough. These results indicate that the CFA sorbent formulation has potential for higher temperature (up to ~800°C) applications, such as molten carbonate fuel cells and combined-cycle power plants employing gas turbines.

CONCLUSIONS

Sorbents prepared in this work with large pore size (0.5-10μm) and relatively high surface area (10-$25m^2/g$) have been found to exhibit improved performance for hot gas cleanup applications over conventional sintered materials. This is displayed by sharp H_2S elution profiles indicating rapid reaction and diffusion rates, and minimal pore plugging, which all result in high absorption capacity, stability and good regenerability of sorbents.

Novel mixed oxide porous sorbents have been synthesized in this work which exhibit improved thermodynamic properties in addition to their physical attributes. For example, the mixed Cu-Fe-Al-O (CFA) sorbent shows much higher H_2S removal efficiency than each of the pure constituents alone. ZnO-containing sorbents have been found to lose zinc during sulfidation (via reduction of ZnO) at temperatures $\geq$600°C. For higher temperature applications the Cu-based sorbents appear to be more attractive. In particular, the CFA sorbent has shown stable and high performance over a variety of sulfidation conditions at 650°C. The H_2S removal efficiency of this sorbent and supporting XRD analysis data correlate well with complex reaction intermediates retaining copper at a higher oxidation state (+2 or +1) with associated better sulfidation equilibria.

Additional, more detailed testing and characterization of these types of sorbents are planned in future work to elucidate the mechanism of high-temperature solid-phase transformations and reactions responsible for the observed sorbent performance and stability.

REFERENCES

1. "Chemistry of Hot Gas Cleanup in Coal Gasification and Combustion," MERC Hot Gas Cleanup Task Force. MERC/SP-78/2, February 1978.

2. "Studies Involving High Temperature Desulfurization/Regeneration Reactions of Metal Oxides for the Fuel Cell Program," Final Report to DOE, Contract No. 31-109- 38-5804, by Giner, Inc., Waltham Massachusetts, February 1981.

3. Westmoreland, P.R., Gibson, J.B. and Harrison, D.P., Environ. Sci. Technol. 11, 488 (1977).

REFERENCES (cont.)

4. Westmoreland, P.R. and Harrison, D.P., Environ. Sci. Technol. 10, 659 (1976).

5. Grindley, T. and Steinfeld, G., "Development and Testing of Regenerable Hot Coal Gas Desulfurization Sorbents," METC, DOE/MC/16545-1125, October 1981.

6. Anderson, G.L. and Garrigan, P.C., "Gas Processing Technology for Integrating Coal Gasifiers with Molten Carbonate Fuel Cells." Paper presented at the Electrochemical Society Meeting, Montreal, Quebec, Canada, May 10-12, 1982.

7. Stegen, G.E., "Development of a Solid Absorption Process for Removal of Sulfur from Fuel Gas," Final Report DE-AC21-79ET11028 Battelle, Pacific Northwest Laboratories, March 1982.

8. Jalan, V., "Studies Involving High Temperature Desulfurization/Regeneration Reactions of Metal Oxides for Fuel Cell Development," Final Report, DOE/MC/16021-1486, October 1983.

9. Flytzani-Stephanopoulos, M., Gavalas, G.R. and Tamhankar, S.S., "Novel Sorbents for High-Temperature Regenerative H_2S Removal," Topical Report to DOE, DOE/MC/20417-3, Jet Propulsion Laboratory, July 1984.

10. Flytzani-Stephanopoulos, M., Gavalas, G.R., Tamhankar, S.S. and Sharma, P.K., "Novel Sorbents for High-Temperature Regenerative H_2S Removal," Quarterly Report to DOE, DOE/MC/20417-4, Jet Propulsion Laboratory, December 1984.

11. Longo, J.M., Horowitz, H.S. and Clavenna, L.R., "A Low Temperature Route to Complex Oxides," Advances in Chemistry Series No. 186, p. 139, American Chemical Society, Washington, D.C., 1980.

12. Singh, B.N., Banerjee, R.K. and Arora, B.R., J. Thermal Analysis 18, 5 (1980).

13. Kolta, G.A., El-Tawil, S.Z., Ibrahim, A.A. and Felix, N.S., Thermochim. Acta 36, 359 (1980).

14. Marcilly, C., Courty, P. and Delmon, B., J. Am. Cer. Soc. 53, No.1, 56 (1970).

15. Barrin, I. and Knacke, O., "Thermochemical Properties of Inorganic Substances," Springer Verlag, 1973.

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