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A NOVEL SUPPORTED SORBENT FOR HOT GAS DESULFURIZATION

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INTRODUCTION

Integrated gasification combined cycle (IGCC) system is one of the most promising power systems for producing electrical energy from coal due to the noticeable improvement in thermal efficiency that it can provide. This advanced power generating system involves the direct contact of hot coal-derived gases with turbine blades. In order to protect the turbines and related equipment from corrosion and abrasion, it is necessary to clean the coal gas. Economical as well as environmental requirements for advanced power generating systems mandate the high-temperature removal of corrosive and abrasive compounds from coal gases such as sulfur and nitrogen containing compounds, trace metals, alkali, residual hydrocarbons, and particulates. Sulfur-containing compounds account for most of the acidic species formed during coal gasification. Hydrogen sulfide, which is the most abundant sulfur-containing compound in coal gas, can react readily with the oxides of alkali earth and transition metals (1).

Westmoreland, et al. (2) reported the results of a thermodynamic screening of the high temperature desulfurization potential of 28 single metal oxides by using the free energy minimization method. Also, kinetic limits for ZnO, MnO, CaO, and V₂O₅ were reported by Westmoreland, et al. (3) for desulfurization reactions. ZnO showed a very favorable thermodynamic equilibrium with H₂S (4) and iron oxide showed easy regenerability with air. Results regarding structural changes in the pure ZnO sorbent at high temperatures were reported by Ranade and Harrison (5). They showed that sintering actually causes the particle to shrink radially, thus for the same number of particles the surface area available for reaction is smaller. Also, zinc metal produced by reduction of ZnO in coal-gas volatilizes above 1290°F (699°C).

Favorable properties of zinc oxide and iron oxide towards absorbing H₂S were combined at the in-house research program of Department of Energy's Morgantown Energy Technology Center. The combined metal oxide sorbent, zinc ferrite, was shown to reduce H₂S levels in gasifier gases to less than 10 ppmv (6). However, zinc ferrite has a temperature limitation. The maximum operating temperature for zinc ferrite is about 1200°F (649°C). Focht, et al. (7) showed that the sorbent lost its pore volume during reduction, and subsequent loss of reactivity was observed during sulfidation. The sorbent also showed a substantial amount of decrepitation above 1200°F (649°C).

Improvements in the original formulation have been attempted in an effort to overcome the limitations of zinc ferrite. An inorganic binder, bentonite, was added to zinc ferrite. Thus, a sorbent with comparable reactivity and capacity to the original sorbent, but with a higher temperature limit than the original zinc ferrite was obtained. This sorbent can withstand temperatures up to 1275°F (691°C), which is not very satisfactory for high temperature fluidized and entrained bed gasifiers.

The need for developing a sorbent having better properties (durability and reactivity) than the original or modified zinc ferrite led researchers to try

other metal oxides. Various combination of metal oxides, such as Zn, Cu, Al, Ti, Fe, Co, Mo, and V were tried at Massachusetts Institute of Technology (MIT) and Jet Propulsion Laboratory (JPL) in an effort to develop a durable and high capacity sorbent for removal of H_2S from hot coal-derived gases (8). Basically, the sorbents tested were divided into two groups: 1. Zinc-based sorbents, 2. Copper-based sorbents. Zinc-based sorbents included zinc ferrite (ZF), zinc-copper ferrite (ZCF), and zinc titanate (ZT). Copper-based sorbents included copper aluminate (CA) and copper-iron aluminate (CFA). Research results (8) showed that zinc-based sorbents were more promising than copper-based sorbents in the temperature range of 1000° - 1350° F (538° - 732°C). One of the most promising sorbents among the zinc-based sorbents was zinc titanate (maximum operating temperature of 1340°F (727°C)). It was found that the TiO_2 phase helps to stabilize the ZnO phase, and volatilization of Zn at temperatures higher than 1290°F (699°C) has been reduced (about 1 wt % Zn is lost in 1000 hours of operation). However, TiO_2 does not absorb H_2S effectively. Therefore, the capacity of zinc titanate is lower than that of zinc ferrite due to dilution effect.

Extrudates of regenerable mixed metal oxide sorbents (copper-modified zinc ferrite, zinc titanate, copper aluminate and copper-iron aluminate) were tested in a high temperature-high pressure (HTHP) fixed bed reactor by Research Triangle Institute (RTI) (9). Reductions in H_2S concentration from >10,000 ppmv to < 1 to 50 ppmv were achieved. The copper-modified zinc ferrite sorbent reduced the H_2S concentration to less than 1 ppmv at up to 1100°F (593°C) with 20 % steam in the gas. The zinc ferrite sorbent was also tested in the same reactor. Zinc titanate outperformed the other mixed metal oxide sorbents in structural strength and capacity at steam levels as low as 5 % and temperatures as high as 1350°F (732°C). However, entrained and fluidized bed gasifiers which are presently being developed have outlet temperatures as high as 1500°F (816°C) to 1800°F (982°C). Furthermore, for continuous desulfurization of a full scale gasification stream, a fluidized bed sorbent system instead of a fixed bed would improve the process efficiency considerably by providing a means for continuous solids regeneration. Zinc ferrite sinters at temperatures higher than 1200°F (649°C). It does not have sufficient attrition resistance to withstand a fluidized bed environment. Zinc titanate can withstand temperatures up to 1350°F (732°C), and has medium strength, but the utilization is low, i.e. 35 - 45 %. Therefore, novel sorbents are still being sought which will show improved resistance to higher temperatures and attrition. Recently, copper manganate sorbents (bulk) are under study by ElectroChem Inc. (10).

The objective of this research is to develop a novel regenerable sorbent which will show improved resistance to higher temperatures and attrition. The potential advantages of supported sorbents, as compared to bulk sorbents, are higher surface area, less resistance for diffusional transport, and higher temperature and attrition resistance. The sorbent investigated in this study is copper and manganese oxides supported on SP-115 zeolite. Results of sulfidation and regeneration experiments conducted using a simulated coal gas mixture at temperatures of 1000° - 1600°F (538° - 871°C) will be reported.

EXPERIMENTAL SECTION

Sorbent Preparation

The sorbents investigated in this study were prepared by a coprecipitation process. SP-115 zeolite (1/8" extrudates, Union Carbide) was used as the support. SP-115 had the following characteristics: SiO_2 > 99 % by weight, surface area = 482 m²/g, crush strength = 6.6 kg/cm, pore diameter = 5.4 Å. The coprecipitation process included: 1) Impregnation of the zeolite with a solution of cupric acetate and manganese acetate in a rotary vacuum evaporator, 2) Dehydration of the sorbent in a vacuum oven at 158°F (70°C) and 0.1 inch Hg, 3) Calcination of the sorbent in a muffle furnace at 1382°F (750°C) for 7 hours. Three samples were

prepared with this process (SP1C5M5, SP2C5M5, and SP2C9M1). The atomic absorption spectrophotometer analysis showed that Cu and Mn loadings on the sorbent SP1C5M5 were 1.82 % and 1.64 % by weight, respectively. SP2C5M5 had 4.39 % by wt. Cu and 6.11 % by wt. Mn. The corresponding values for SP2C9M1 were 5.15 % and 5.73 % by weight, respectively. The uncertainty in the atomic absorption analysis is $\pm 1\%$.

Experimental

A schematic diagram of the experimental system is shown in Figure 1. The system consisted of a gas mixing system, a fixed bed reactor, a condenser and a water knock-out pot, a gas sampling system, and a tail-gas cleanup system. Gases were supplied from gas cylinders and the flow rates were monitored through mass flow controllers. After the gases were mixed in a manifold, they were fed into the fixed bed reactor. This gas mixture simulated the partially quenched exit gas of an air-blown KRW fluidized bed coal gasifier which had the following molar composition: 42.5 % N_2 , 11 % CO_2 , 12.5 % CO , 13.8 % H_2 , 1 % CH_4 , and 0.2 % H_2S . 19 % H_2O in the gas mixture was provided by adding a predetermined amount of water into the gas stream before it entered the reactor via a high pressure pump.

The reactor which consisted of a zirconia tube, with 0.875-inch inside diameter and 12-inch length, was placed vertically in an electric furnace equipped with graphite heating elements. The furnace was water cooled. The graphite heating elements were located in a helium atmosphere to protect them from oxidation. The temperatures of the gas at the inlet and the center of the reactor were measured by K-type thermocouples located along the central axis. The reactor was designed to withstand a pressure of 15 psig and a temperature of 3000°F (1649°C). The sorbent sample was placed in the center of the reactor and the bed height was 2 inches. The gas lines between the reactor outlet and the condenser inlet were heated via heating tapes and heavily insulated to prevent the condensation of steam in the gas lines. The exit gas from the reactor was filtered, cooled down in the condenser, and sampled for gas analysis. The tail gas was sent through the absorbers to remove the sulfurous gases before it was discharged to the atmosphere.

The experiments consisted of a sequence of sulfidation and regeneration runs. The reactor temperature was held constant during the sulfidation and regeneration experiments. Reactor pressure was maintained at 5 ± 3 psig. Three temperatures were tested: 1000, 1250, and 1600° F (538°, 677°, and 871°C). The space velocities for the sulfidation and the regeneration runs were 2000 and 600 hr^{-1} , respectively. Regeneration of the sulfided sorbent was conducted with air only and with a 50 % air/50 % steam mixture. Breakthrough during sulfidation runs was defined as 200 ppmv H_2S in the effluent gas. After the sulfidation run was stopped, the reactor was purged with nitrogen for at least 15 minutes. Regeneration was carried out at the reaction temperature. The regeneration cycle was stopped when the SO_2 concentration of the effluent gas was below 500 ppmv. The sorbents were subjected to five sulfidation/regeneration cycles to establish sulfur sorption capacity and regenerability.

Selected sorbent samples were analyzed for total weight, metal and sulfur content, crush strength, surface area, average pore diameter, pore volume, and pore size distribution both before and after reaction. Gas grab samples obtained during experimentation were analyzed by gas chromatography. Also Gas-tech precision gas detection tubes were used to determine the H_2S and SO_2 concentrations in the inlet and outlet gas streams.

RESULTS AND DISCUSSION

The effect of temperature on sorbent capacity is shown in Figure 2. The H_2S breakthrough curves indicate that the breakthrough times were 37, 45, and 45 minutes at 1000°F (538°C), 1250°F (677°C), and 1600°F (871°C), respectively. The

sorbent has greater capacity at 1250°F (677°C) and 1600°F (871°C) than at 1000°F (538°C). However, the prebreakthrough H_2S levels are lower at 1000°F (538°C) and 1250°F (677°C) than at 1600°F (871°C). Although the prebreakthrough H_2S level is lower at 1000°F (538°C), the sorbent has more total capacity at the higher temperatures.

Two runs were conducted at 1250°F (677°C) with different samples from the same batch of SPIC5M5 sorbent, to establish the extent of reproducibility of the experimental method. Twelve detector tube readings of H_2S were taken, 5 min apart, for each run. The average difference between readings for the two runs was 30 ppmv. Thus, the experimental method appears to be reasonably reproducible.

Sorbent regenerability was tested at 1250°F (677°C). Two and one-half cycles were conducted with only air as the regenerant gas, and five cycles were studied using a 50 mole % steam/50 mole % air mixture for regeneration. Two criterion were used to assess the regenerability of the sorbent: (1) a comparison of the H_2S breakthrough curves, and (2) a comparison of the SO_2 outlet curves during the sulfidations.

When the sorbent was regenerated with air, the second and third sulfidation breakthrough curves were somewhat similar. However, the prebreakthrough average H_2S outlet concentration was approximately 50 ppmv less for the third sulfidation than for the second sulfidation. Figure 3 shows the H_2S breakthrough curves after the sorbent was regenerated with steam/air. The curve for the first sulfidation was not shown, as the reactor bypass was accidentally left open during the run. The third through sixth sulfidations, conducted with steam/air regeneration, gave similar breakthrough curves. Thus, the steam/air regeneration appears to give better regenerability than air regeneration.

Outlet SO_2 concentrations were compared for the second and third sulfidations (set I) using air regeneration, with the second, third, and fourth sulfidations (set II) using steam/air regeneration. After 15 min on-stream, set I showed outlet SO_2 concentrations between 500 and 600 ppmv. After the same period, set II yielded SO_2 concentrations ranging between 30 and 450 ppmv. These results indicate that more sulfate was formed during air regeneration than during steam/air regeneration. This is not unexpected, since the presence of steam reduces the overall oxidative properties of the regenerant stream. In general, if SO_2 is released in large quantities when reducing gases are introduced after oxidative regeneration, this indicates that sulfates have been formed during the regeneration. The release of such sulfurous gases must be avoided during sulfidation. It has been suggested in studies on zinc ferrite that a clean reducing gas could be used for reductive regeneration of the sorbent after oxidative regeneration, and prior to sulfidation. However, the economics for carrying out a reductive regeneration step are poor, due to the capital cost of additional vessels and the introduction of complications into the overall operation of the system (11).

Although no carbonyl sulfide was fed to the reactor in the simulated gas mixture, appreciable concentrations were detected in the outlet gas during sulfidation. The COS concentration was usually greater than 50 ppmv, and often as high as 100-250 ppmv in the outlet gas. It is well known that certain zeolites can catalyze the COS formation reactions. CO and CO_2 can react with H_2S according to the following reactions (12):



At temperatures between 440°F (227°C) and 1340°F (727°C), the thermodynamics of reaction [2] are more favorable than those of reaction [1]. Figure 4 shows that COS production became a minimum after about 30-40 min on-stream, and then

increased. The initial decrease in COS may have been due to reduced availability of CO, because of the competing reactions in which CO reduces copper oxides. The later increase in COS formation may have been caused by the kinetic effect of gradual heating of the sorbent bed with time on-stream. The effect of increased temperature on COS formation can be seen in Figure 5. It appears that 1250°F (677°C) is a more favorable temperature for COS formation than either 1000°F (538°C) or 1500°F (816°C). The figure also suggests that COS production may increase with the number of cycles; other data which were collected support this conclusion.

The effect of a single loading of the metal acetate solution versus a double loading of the metals is shown in Figure 6. As expected, the double-coated sorbent, SP2C5M5, has a breakthrough time that is nearly double that of the single-coated SP1C5M5. Thus, the capacity of the sorbent extrudates can be increased via multiple loadings of the metal salts.

Sorbents SP2C5M5 and SP2C9M1 were also compared for their ability to remove H₂S from the simulated coal gas mixture. The second and third sulfidations of each sorbent are shown in Figure 7. The SP2C9M1 sorbent appears to have greater capacity than SP2C5M5 for H₂S removal.

The surface area of the sorbent was determined before and after the reaction by using the Langmuir adsorption method, with a maximum error of $\pm 1.5\%$. The fresh SP-115 zeolite without metal coating had an average surface area of 482 m²/g. The unreacted SP1C5M5 had an average surface area of 434 m²/g, with a metal loading of 1.82 wt % Cu and 1.64 wt % Mn. This suggests that the presence of the metal has caused some pore blockage. After single sulfidations at 1000°F (538°C), 1250°F (677°C), and 1600°F (871°C), the surface area decreased to 379, 370, and 237 m²/g, respectively. The loss of surface area under reaction conditions may be due to coalescence of pores of the zeolite, or to a certain extent, silicic acid formation by reaction of the zeolite with high-temperature steam.

For a 5-cycle set of experiments on sorbent SP2C5M5, the utilization of sorbent at breakthrough for each of the first through fifth sulfidations was, respectively, 20%, 7%, 7%, 13%, and 12%. These percent utilizations were calculated using the following assumptions: (1) the H₂S breakthrough point was 200 ppmv H₂S in the outlet gas, (2) the metal composition of the sorbent was 4.39 wt % Cu and 6.11 wt % Mn, as determined by atomic absorption analysis, (3) the concentration of H₂S in the inlet gas was 2000 ppmv, and (4) the sulfided metals in the sorbent were present only in the form of Cu₂S + MnS. The decrease in sorbent utilization after the first sulfidation was due to incomplete regeneration. The increase between 7% and 12-13% may have been due to random variations. It is possible that the relatively low utilization of the sorbent was caused by ineffective coating of the zeolite pores, i.e., the metals were deposited in several atomic layers on the outer surface of the extrudate, rather than inside the pores. Or, even if the pores were effectively coated, there may have been significant resistances to diffusion of H₂S into the pores.

Six different samples of the bed material from the 5-cycle set performed with SP2C5M5 at 1250°F (677°C) and the 3-cycle set run with SP2C9M1 at 1250°F were analyzed using atomic absorption. There was no conclusive evidence for loss of Cu or Mn greater than a few percent. Thus, these metals do not appear to undergo appreciable volatilization under these conditions of sulfidation and regeneration.

The crush strength of the sorbent extrudates is an important consideration for practical operation. Crush strength was determined by taking the average of the force per unit length of extrudate required to crush 15 extrudates; the range of error for these tests is ± 20 -35%, within the first standard deviation. The fresh SP-115 zeolite without metal coating had an average crush strength of 6.58 kg/cm. The crush strength for fresh SP2C5M5 and SP2C9M1 were 29.6 and 11.1 kg/cm, respectively. The metal coating makes the extrudates much stronger; particularly

the Mn appears to promote increased resistance to crushing. The average crush strength of 6 samples from the SP2C5M5 bed, after 5 cycles, decreased by only 6%. The average crush strength of 5 samples from the SP2C9M1 bed, after 3 cycles, increased by 3%. Therefore, the crush strength of the zeolite was increased by the metal loading, and essentially unchanged by reaction.

CONCLUSIONS

For the temperature range of 1000°-1600°F (538°-871°C), the SP-115 zeolite-supported Cu/Mn oxides sorbent had more total capacity at 1250°F (677°C) and 1600°F (871°C) than at 1000°F (538°C). Regeneration with a 50 mole % steam/50 mole % air mixture was preferred over air regeneration, due to decreased sulfate formation in the presence of steam. Further studies would be required to optimize regeneration conditions, so that minimal sulfate is formed during oxidative regeneration. Appreciable amounts of COS were formed at 1250°F (677°C), probably due to reactions catalyzed by the zeolite; however, at 1500°F (816°C) the production of COS greatly decreased. The sorbent containing Cu:Mn molar ratios of 9:1 had greater capacity for H₂S than those containing equimolar ratios of the metals. Sorbent utilization with repeated sulfidation/regeneration cycles was low (<13% for SP2C5M5). Surface area of the sorbent decreased with metal loading and with reaction temperatures between 1250°F (677°C) and 1600°F (871°C). It is uncertain whether the zeolite pores had been effectively coated or plugged by the metal acetate solutions during preparation. There was little or no volatilization of the metals at 1250°F (677°C). The SP-115 zeolite will require further testing to determine whether it can withstand the highest temperatures (1250°-1600°F) (677°-871°C) for multiple cycles.

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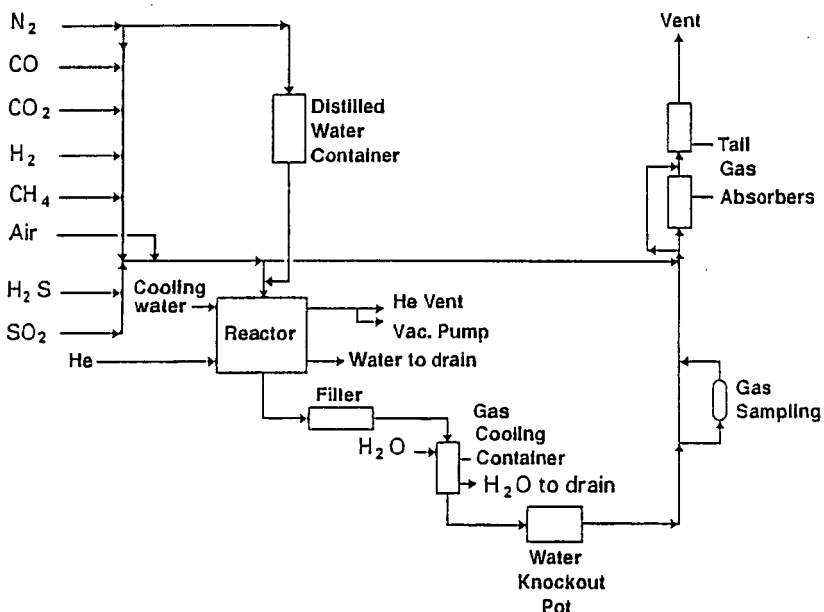


Fig. 1 Flow diagram of fixed bed reactor system

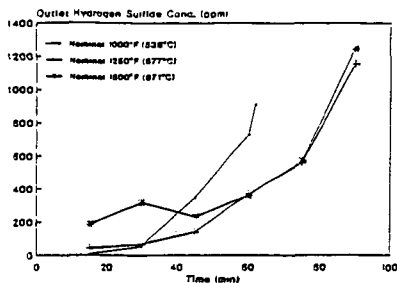


Fig. 2 Hydrogen sulfide breakthrough curves for single sulfidations of SPICSM5 sorbent: The effect of temperature

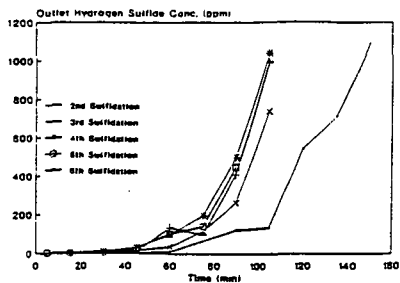


Fig. 3 Hydrogen sulfide breakthrough curves for multiple sulfidations of SP2CSM5 sorbent at nominal 1250°F (677°C) with 50 mole % steam/50 mole % air used for regeneration: Regenerability

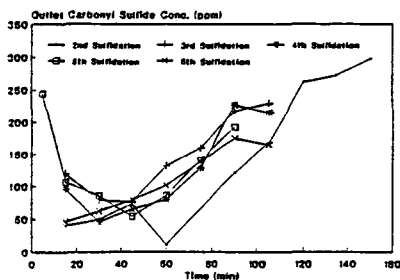


Fig. 4 Outlet concentrations of carbonyl sulfide for multiple sulfidations of SP2CSM5 sorbent at nominal 1250°C (677°C) with 50 mole % steam/50 mole % air used for regeneration: The effect of cycle number (after steam/air regeneration) on carbonyl sulfide formation

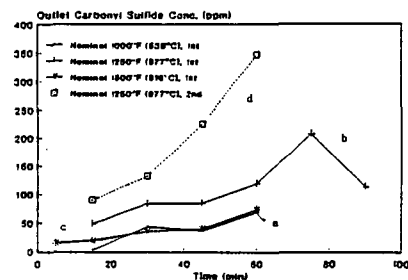


Fig. 5 Outlet concentrations of carbonyl sulfide for sorbent SPICSM5 for (a-c) single sulfidations, and (d) a second sulfidation after air regeneration: The effect of temperature and cycle number (after air regeneration) on carbonyl sulfide formation

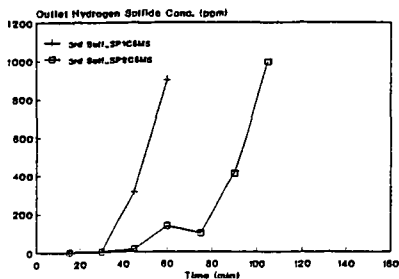


Fig. 6 Hydrogen sulfide breakthrough curves for the third sulfidation of sorbents SPICSM5 and SP2CSM5 at nominal 1250°F (677°C): The effect of the number of metal loadings

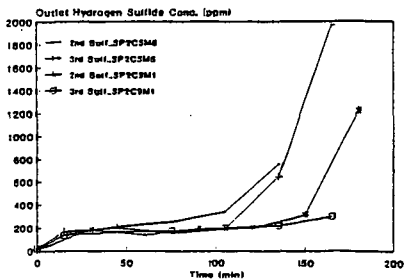


Fig. 7 Hydrogen sulfide breakthrough curves for the second and third sulfidations of sorbents SP2CSM5 and SP2CSM1 at nominal 1250°F (677°C): The effect of nominal molar ratios of Cu:Mn of 3:1 versus 9:1