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REACTIVITY OF METAL OXIDE SORBENTS FOR REMOVAL OF SULFUR COMPOUNDS FROM COAL GASES AT HIGH TEMPERATURE AND PRESSURE

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ABSTRACT

Hot-gas desulfurization for the integrated gasification combined cycle (IGCC) process has been investigated to effectively remove hydrogen sulfide with various metal oxide sorbents at high temperatures and pressures. Metal oxide sorbents such as zinc titanate oxide, zinc ferrite oxide, copper oxide, manganese oxide, and calcium oxide were found to be promising sorbents in comparison with other removal methods such as membrane separation and reactive membrane separation. The removal reaction of H_2S from coal gas mixtures with zinc titanate oxide sorbents was conducted in a batch reactor. The main objectives of this research are to formulate promising metal oxide sorbents for removal of hydrogen sulfide from coal gas mixtures, to compare reactivity of a formulated sorbent with a sorbent supplied by the Research Triangle Institute at high temperatures and pressures, and to determine effects of concentrations of moisture contained in coal gas mixtures on equilibrium absorption of H_2S into metal oxide sorbents. Promising durable metal oxide sorbents with high-sulfur-absorbing capacity were formulated by mixing active metal oxide powders with inert metal oxide powders and calcining these powder mixtures.

INTRODUCTION

Coal is a principal energy resource in the United States and continues to be the major fuel utilized by electrical power plants. The coal resources will become attractive for chemical feedstocks as well as for a source of liquid and gaseous fuels as petroleum resources become continually depleted.

Coal is a very complex and heterogeneous material. Effective utilization of coal requires an understanding of the formation, structure, and purification of coal. Raw coal consists of minerals and organic matter. The minerals include primarily pyrites, silicate (quartz, clays), and various minor minerals, whereas organic matter is composed of carbon, oxygen, hydrogen, nitrogen, and sulfur. Sulfur in coal is present in organic, pyritic, and sulfate forms. Although the sulfur occurring in the form of relatively coarse pyrite particles is removed largely by density separation, very finely disseminated pyrite and organic sulfur cannot be removed in this way. Sulfur products from combustion not only pollute the environment, but are also detrimental to combustion systems because of the corrosive action of their combustion products. In the gasification process, coal is reacted with steam and oxygen to produce a medium-to high-calorific-value fuel gas. The fuel gas can be subsequently combusted in a gas/steam turbine combined cycle (IGCC). These IGCC-based power generation options offer much higher thermodynamic cycle efficiencies that promise to remove all forms of pollutants released from a coal conversion process through lower fuel consumption.

The removal of hydrogen sulfide from hot coal gas produced in the IGCC- based system by metal oxide sorbents is required to protect downstream combustion turbines from being corroded with sulfur compounds. The removal of sulfur compounds from coal gas products is investigated by using various metal oxide sorbents and membrane separation methods. Current investigations show that the removal of sulfur with metal oxide sorbents appears to deliver the most promising results. The main requirements of these metal oxide sorbents are durability and a high sulfur-loading capacity during absorption-regeneration cycles. The spalling of sulfur-loaded fixed-bed metal oxide sorbents occurs during the regeneration of sulfur-loaded metal sorbents. The main causes of spalling of sorbents appear to be the temperature rise of sulfur-loaded sorbents due to tremendous exothermic heat of reaction and sulfate formation during the regeneration process. Sulfate products occupy more space than sulfide products in pores of sorbents and result in significant structural stresses of metal sorbents. The main objectives of this research are to formulate promising metal oxide sorbents for removal of hydrogen sulfide from coal gas mixtures, to compare reactivity of the formulated sorbent with a sorbent supplied by the Research Triangle Institute at high temperatures and pressures, and to determine effects of concentrations of moisture in coal gas mixtures on equilibrium absorption of H_2S into metal oxide sorbents.

BACKGROUND

In the United States, coal is currently used to produce approximately 55 percent of the country's electricity. Coal-burning electric utilities throughout the country must comply with increasingly stringent environmental regulations. Coal gasification is a process in which coal is used to produce a clean fuel gas which, in turn, is burned to generate power. Because most pollutants (such as sulfur) are removed prior to the combustion process, the fuel gas can be burned in an environmentally acceptable manner [1].

Interest in the integrated gasification combustion cycle (IGCC) in the utility industry is increasing because these systems have the ability to generate power with coal in a manner that is more efficient with lower air emissions than conventional pulverized-coal-fired units utilizing flue gas desulfurization [2]. In the gasifier, coal rapidly produces a gas mixture of carbon monoxide, carbon dioxide, methane, hydrogen, water vapor, and nitrogen as well as hydrogen sulfide, ammonia, and other trace impurities. In the reducing environment of the gasifier nearly all of the sulfur present in the coal converts to hydrogen sulfide before it reacts with sorbents [3]. Hydrogen sulfide pollutes environments and corrodes downstream power-producing facilities such as turbines and transfer pipelines.

Various metal oxides were found to be useful in the removal of sulfur compounds in coal gas mixtures. The reactions of metal oxides with sulfur-containing compounds, such as SO_2 and H_2S, are extensively investigated in controlling emissions of gaseous pollutants from coal utilization systems. Limestone and dolomite are used in the control of emissions of sulfur dioxide from the coal-fired power plants. In the high-temperature environment of a combustor, the limestone or dolomite particles undergo calcination. The calcined product (CaO or MgO) then reacts with the sulfur dioxide produced during coal combustion, primarily forming calcium or magnesium sulfate. Alternatively, calcium oxide and other metal oxide sorbents (iron oxide, zinc oxide, zinc ferrite, zinc titanate, etc.) are used to remove sulfur-containing compounds (predominantly H_2S) from hot coal gases. An important difference exists between their reaction with H_2S and with SO_2. The sulfide produced during reaction with H_2S occupies less space than the solid product produced during sulfation and, as a result, complete pore closure in the case of sulfidation can happen only for low initial porosity [4].

Advanced integrated gasification combined cycle (IGCC) power systems require the development of high-temperature metal oxide sorbents that are both durable and regenerable and which are capable of removing hydrogen sulfide (H_2S) from coal gasifier gas down to very low levels, typically less than 20 ppmv. For example, zinc ferrite and zinc titanate are leading regenerable sorbent candidates [5]. Many researchers characterize the durability, regenerability, and sulfur capacity of metal oxide sorbents with simulated coal gas mixtures as well as regenerating gas mixtures at high temperatures and pressures using various reactor configurations such as batch reactors and continuous differential reactors as well as fixed-bed, moving-bed, and fluidized-bed reactors.

Fluidized-bed reactors offer several potential advantages over fixed-bed reactors. These advantages include excellent gas-solid contact, ability to continuously add or remove sorbent, excellent temperature control of the highly exothermic regeneration, use of small particles leading to faster overall kinetics, and continuous steady-state operation. However, fluidized beds require highly attrition-resistant sorbents with good sulfur capacity that are capable of withstanding the stresses induced by fluidization and transport as well as rapid temperature swings and chemical transformations before they can be successfully employed [6].

Mixed metal oxide sorbents are investigated to improve mechanical stress during cyclic absorption and regeneration processes at high temperatures and high pressures. Both molybdenum oxide as a porosity modifier and calcium sulfate as a binder are used to improve the durability of the sorbents. The use of these additives results in enhancements of the mechanical properties of the fresh materials and minimizes the occurrence of spalling of the pellets over extended multicycle testing under moving-bed hot gas cleanup conditions [7].

The durability of zinc ferrite sorbents as one of the leading regenerable sorbent candidates was examined by Gupta [5]. Excessive sorbent loss was observed at a sulfidation temperature of 625°C. It is thought that the attrition of the sorbent in the reactor is primarily due to chemical transformations rather than mechanical forces. Possible chemical transformations responsible for the attrition are excessive reduction of $ZnFe_2O_4$ and iron carbide formation. The applicability of zinc ferrite as a hot-gas desulfurization sorbent, therefore, is conservatively limited to below 550°C and to moderately reducing coal gases [6].

Recent batch-mode sulfidation tests at 285 psig and 1,200°F demonstrated that the prospects for developing an effective fluid-bed hot-gas desulfurization system are promising. A H_2S removal of greater than 99 percent was consistently shown with a sorbent utilization of up to 25 percent. However, the regeneration reaction in the batch reactor occurs too rapidly at 1,400 °F; therefore, any useful kinetic data on regeneration of a sorbent of 70-300 mm particles cannot be obtained [8].

Dolomite is used to remove the bulk of sulfur in the fluidized-bed gasifier. Hydrogen sulfide reacts with calcium carbonate and/or calcium oxide, forming calcium sulfide. Calcium sulfide is stabilized by oxidizing it to calcium sulfate within the gasfier for safe disposal. The crushed coal reacts with air and steam at a temperature of 1,650-1,840°F. The temperature within the fluidized bed must be controlled to maintain a non-slagging condition for the ash [3].

Many researchers have investigated the reactivity of metal oxide sorbents [9,10,11,12,13], including the reaction pathways during sulfidation as well as the regeneration of metal oxide sorbents. When calcining mixtures of ZnO and TiO_2 powders at high temperatures, three crystalline structures of zinc titanate may form, depending on the ratio of zinc to titanium: $ZnTiO_3$, $Zn_2Ti_3O_8$, or Zn_2TiO_4. Zinc titanate (Zn_2TiO_4) has the highest zinc-to-titanium molar ratio and would be the most desired crystalline phase because of its higher sulfur capacity. For this case, the overall reactions occurring during H_2S absorption from coal gases and regeneration with diluted air are as follows:

$$\text{Absorption Reaction:}\quad Zn_2TiO_4 + 2H_2S \rightarrow 2ZnS + TiO_2 + 2H_2O$$

$$\text{Regeneration Reaction:}\quad 2ZnS + TiO_2 + 3O_2 \rightarrow Zn_2TiO_4 + 2SO_2$$

In addition to absorption and regeneration reactions, zinc sulfate formation may occur during regeneration below 1,200°F and at high O_2 and SO_2 concentrations. Zinc sulfate formation is undesired because the sulfate occupies more volume than the sulfides in the pores (producing more internal pellet stresses) and decomposes during subsequent absorption releasing SO_2 [14].

Only the ZnO component of the zinc titanate sorbent reacts with H_2S while the TiO_2 provides the stability to the sorbent against ZnO reduction by the CO and/or H present in the coal gas. Hence, the sulfur absorption capacity of zinc titanate sorbents [15,16,17,18,19] is significantly lower than zinc ferrite sorbents [6]. No significant losses in zinc for the 2:1 (Zn:Ti) formula of zinc titanate were measured at the absorption temperature of 1,000 °F. However, zinc metal sublimation is known to be significant at higher temperatures (e.g.>1,300 °F) [14].

The effects of temperature on the stability and reaction pathways of metal oxide sorbents were investigated during both the absorption reactions and the regeneration reactions of sorbents. Regeneration of sulfided zinc titanate is a highly exothermic reaction. The desirable reaction occurs with an enormous heat of reaction (-70.7 kcal/mol of O_2 consumed). To prevent excessive temperature rise that may lead to sorbent sintering, an air diluent mixture (typically air-steam or air-nitrogen) is used for the regeneration with an oxygen concentration of about 1 to 5 volume percent. However, if regeneration is not carried out at a sufficiently high temperature, a competing sulfation reaction may occur, leading to incomplete regeneration. A temperature of 760 °C was found to be ideal for preventing both sulfate formation and excessive surface area loss due to sorbent sintering [6].

EXPERIMENTAL

The main objectives of this research are to formulate promising metal oxide sorbents for the removal of hydrogen sulfide from coal gas mixtures, as well as to determine effects of concentrations of moisture in coal gas mixtures on equilibrium absorption of H_2S into metal oxide sorbents, and to compare reactivity of a formulated sorbent with a sorbent supplied by the Research Triangle Institute at high temperatures and pressures.

Fresh metal oxide sorbent particles with promising formulas and simulated coal gases containing hydrogen sulfide are introduced in a batch reactor. The volume of the batch reactor is 35 cm^3. It is fabricated with 316 stainless steel (SS) metal. Fine metal oxide sorbents are used to minimize effects of intraparticle diffusion of hydrogen sulfide through sulfided sorbent particles. After loading the batch reactor with a fresh sorbent and a simulated coal gas mixture, it is then submerged in a constant-temperature fluidized sand bath to maintain the heterogeneous reaction system at a desired reaction temperature. It is also shaken in the sand bath to reduce effects of mass transfer of hydrogen sulfide to sorbent particles. The sulfidation reaction is then terminated at a desired reaction duration. Conversions of sorbents are analyzed with an electronic balance and a gas chromatograph.

Initial experiments on formulating metal oxide sorbents were performed, using flour powder as an organic burnout, zinc oxide powder as an active sorbent ingredient, bentonite as a binding material, and titanium oxide as a supporting metal oxide, as shown in TABLE 1. This pastry mixture was extruded as 1-mm cylindrical rods. The viscosity of the pasty mixture appeared to be sensitive to amounts of distilled water as well as amounts of flour added to the powder mixture. Homogeneous mixing of this pasty slurry mixture seemed to be very important in producing duplicate formulations of sorbents. The TU-1 and TU-2 sorbents were calcined for 2 hours at 800°C.

DISCUSSION

The ZT-4 sorbent was formulated and supplied by the Research Triangle Institute. This sorbent has a nominal chemical composition of Zn:Ti of 1.5 with a bentonite binder of 5 wt %. The nominal particle size of the ZT-4 sorbent is in the range of 100 to 400 μm, as shown in TABLE 2. In comparison, the TU-1 sorbent was formulated at our laboratory. The formulation composition as well as some physical properties of the TU-1 sorbent are shown in TABLE 1. Experiments on reactivity of the ZT-4 sorbent, experiments on reactivity of the 1-mm-cylindrical-rod TU-1 sorbent, and experiments on durability of the ZT-4 sorbent as well as TU-1 sorbent were performed in the presence of hydrogen sulfide, hydrogen, and moisture in a newly fabricated 35-cm^3 316 SS batch reactor.

Experiments on reactivity of hydrogen sulfide contained in a simulated coal gas mixture with the 316 SS batch reactor wall were carried out, as shown in TABLE 3 and FIGURE 1. The simulated coal gas mixture consists of 9107 ppm hydrogen sulfide (0.005 g; 1 wt %), 0.085 g water (15.84 wt %), 0.0029 g hydrogen (0.58 wt %), and 0.4046 g nitrogen (81.34 wt %). These experimental data were used in evaluating equilibrium absorption as well as reactivity of H_2S into metal oxide sorbents with the aid of changes

TABLE 1. FORMULATION OF METAL OXIDE SORBENTS.

	TU-1	TU-2
ZnO, g	1	1
TiO_2, g	2	2
Bentonite, g	0.1	0.3
Flour, g	0.3	0.6
Water, g	2.0	3.5
Calcination Temperature, °C	800	800
Calcination Duration, min	120	120
Density of Sorbent, g/cm^3	1.73	
Specific Pore Volume, cm^3/g	0.36	

TABLE 2. PHYSICAL PROPERTIES OF THE ZT-4 SORBENT, FORMULATED WITH 5 wt% BENTONITE AT THE NOMINAL Zn TO TI RATIO OF 1.5, CALCINED FOR 2 HOURS AT 825 °C.

Particle Size Distribution		
Mesh Size	μm	wt %
+ 50	+297	14.70
- 50+ 60	-297+250	14.10
- 60+ 80	-250+177	26.10
- 80+100	-177+149	11.50
-100+120	-149+125	12.80
-120+140	-125+105	9.00
-140+170	-105+ 89	11.70

Average Particle Diameter, μm	180-200
Medium Pore Diameter, Å	1972
Mercury Pore Volume, cc/g	0.2050
Particle Density, g/cc	2.35
BET Surface Area, m^2/g	3.28

TABLE 3. EXPERIMENTAL CONDITIONS FOR THE REACTION OF HYDROGEN SULFIDE WITH 316 STAINLESS STEEL BATCH REACTOR WALL AT VARIOUS TEMPERATURES.

Reactor Volume, cm^3	35
Temperature, °C	350 - 500
Reaction Time, min	5 - 60
Initial Partial Pressure of Hydrogen at 25°C, kPa	101.3
Initial Amount of Water, g	0.085
Initial Concentration of H_2S, ppmv	9107
Initial Partial Pressure of Nitrogen at 25°C, kPa	1033.7

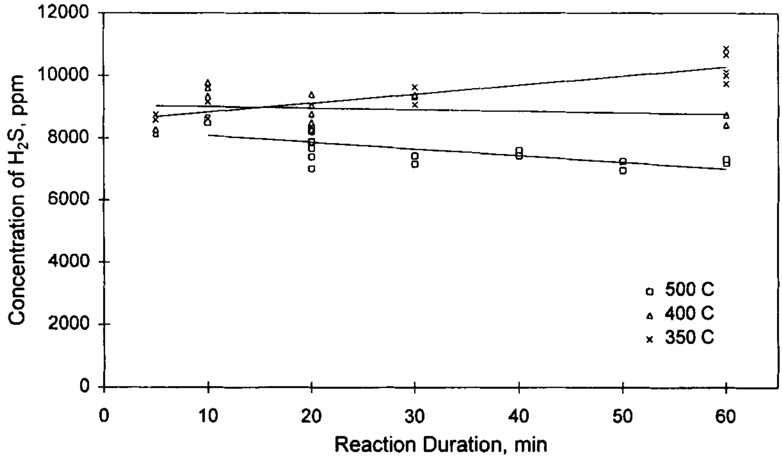

FIGURE 1. Reactivity of 316 stainless steel with the initial concentration 9107 ppm H_2S in the presence of 0.085 g moisture at various temperatures.

in concentrations of H_2S in the micro batch reactor. Absorption of hydrogen sulfide into the reactor wall increases with absorption temperatures. Absorption of H_2S into the 316 SS wall increases with absorption durations above 400°C. However, absorption of H_2S into the 316 SS wall does not take place at 350°C, and previously absorbed H_2S appears to be released from the 316 SS wall at 350°C. In this way, concentrations of H_2S increase with reaction durations at 350°C. The concentration of H_2S at the 60-min absorption duration is higher than the initial concentration of H_2S.

A series of experiments on effects of varying amounts of the ZT-4 sorbent on removal of H_2S were carried out for 10 min at 500°C (see TABLE 4 and FIGURE 2). Removal of H_2S increases with amounts of the sorbent but appears to level off above 0.1 g sorbent. These observations may suggest that equilibrium concentration of H_2S with the sorbent at 500°C is independent of amounts of the sorbent in the micro batch reactor.

Reactivity of the ZT-4 sorbent with H_2S was examined at 350 - 500°C as shown in FIGURE 3. Reactivity of the sorbent increases with reaction temperatures. Equilibrium

TABLE 4. EXPERIMENTAL CONDITIONS FOR THE REACTION OF HYDROGEN SULFIDE WITH ZT-4 SORBENT AT VARIOUS TEMPERATURES.

Reactor Volume, cm^3	35
Temperature, °C	350 - 500
Reaction Time, min	1 - 60
Particle Size	200 μm or <127 μm
Amount of Sorbent, g	0.1
Initial Partial Pressure of Hydrogen at 25°C, kPa	101.3
Initial Amount of Water, g	0.085 - 0.120
Initial Concentration of H_2S, ppmv	9107
Initial Partial Pressure of Nitrogen at 25°C, psia	1033.7

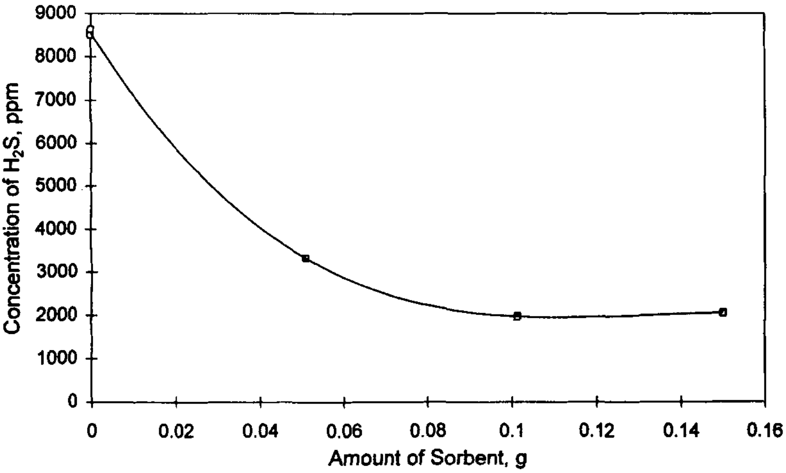

FIGURE 2. Effects of ZT-4 sorbent amounts on removal of H_2S with the initial concentration 9107 ppm H_2S in the presence of 0.085 g moisture for 10 min at 500°C.

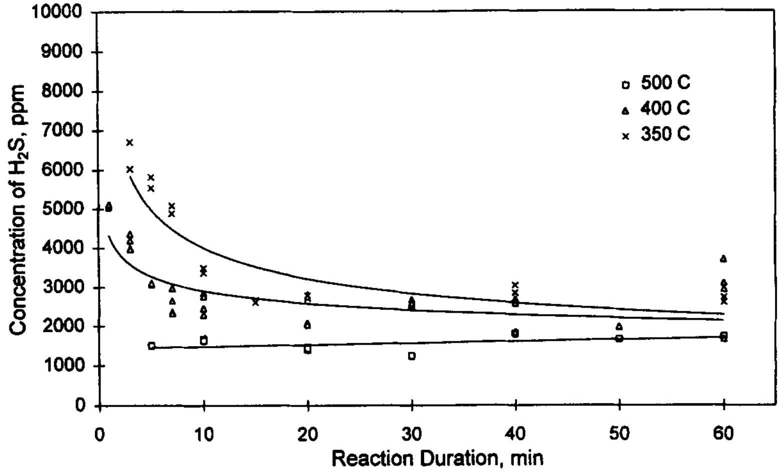

FIGURE 3. Reactivity of 0.1 g ZT-4 sorbent with the initial concentration 9107 ppm H_2S in the presence of 0.085 g moisture at various temperatures.

absorption of H_2S into the sorbent increases with increased reaction temperatures and requires longer reaction durations with lower reaction temperatures.

Effects of moisture on reactivity of the 200-micron ZT-4 sorbent with H_2S were investigated for 3 min at 350°C as shown in FIGURES 4 and 5. Increased moisture increases removal of H_2S below equilibrium absorption at 350°C as shown in FIGURE 4. These experimental data may suggest that dynamic absorption of H_2S into the sorbent is affected by moisture quantities in the reactor.

FIGURE 5 shows that equilibrium absorption of H_2S appears to be independent of the amount of moisture. This fact may indicate that moisture does not affect equilibrium absorption of H_2S into the ZT-4 sorbent at 350°C, but affects dynamic absorption of H_2S into the ZT-4 sorbent.

Reactivity of the 1-mm-cylindrical-rod TU-1 sorbent, the first sorbent formulated at our laboratory, was tested at 350°C, as shown in TABLE 5 and FIGURE 6. This sorbent, consisting mainly of zinc oxide and titanium oxide, was formulated with a physical

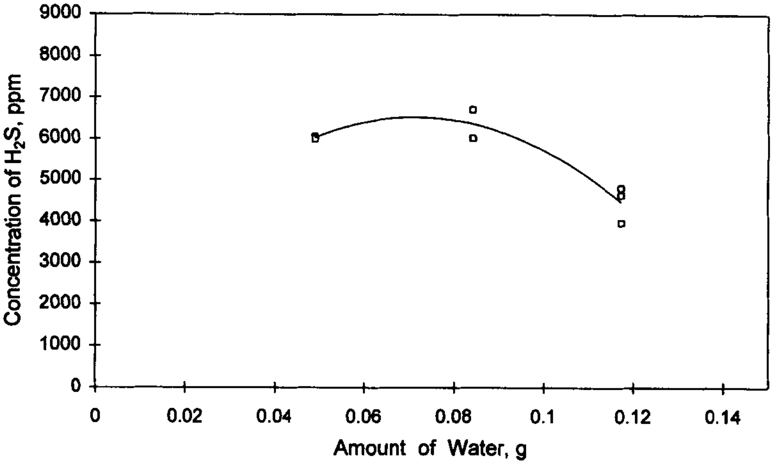

FIGURE 4. Effects of moisture on reactivity of 0.1 g ZT-4 sorbent with the initial concentration 9107 ppm H_2S for 3 min at 350°C.

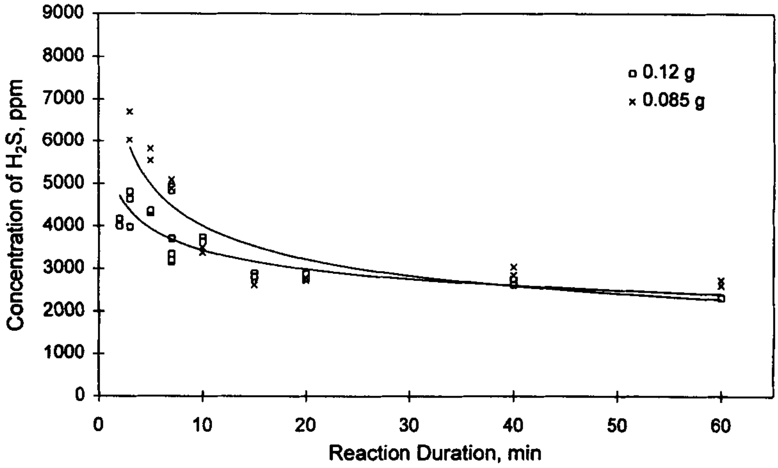

FIGURE 5. Effects of moisture on reactivity of 0.1 g ZT-4 sorbent with the initial concentration 9107 ppm H_2S and various moisture amounts at 350°C.

TABLE 5. EXPERIMENTAL CONDITIONS FOR THE REACTION OF HYDROGEN SULFIDE WITH TU-1 SORBENT AT VARIOUS TEMPERATURES.

Reactor Volume, cm^3	35
Temperature, °C	350 - 500
Reaction Time, min	1 - 15
Particle Size, μm	<127
Amount of Sorbent, g	0.1
Initial Partial Pressure of Hydrogen at 25°C, kPa	101.3
Initial Amount of Water, g	0.085
Initial Concentration of H_2S, ppmv	9107
Initial Partial Pressure of Nitrogen at 25°C, kPa	1033.7

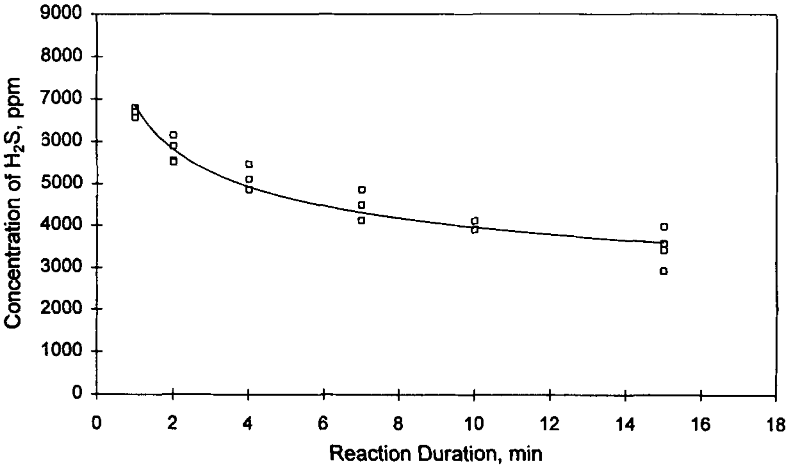

FIGURE 6. Reactivity of 0.1 g TU-1 sorbent with the initial concentration 9107 ppm H_2S in the presence of 0.085 g moisture at 350°C and various reaction durations.

mixing method, as mentioned in the experimental section. Absorption of H_2S into the TU-1 sorbent also increases with absorption durations below equilibrium absorption, as shown in the experimental data of the ZT-4 sorbent.

Effects of particle sizes of the ZT-4 sorbent on the removal of H_2S were examined at 350 °C as shown in FIGURE 7. The minus-127-µm (micron) ZT-4 sorbent removes more H_2S than the 200-µm (micron) sorbent below equilibrium absorption. Equilibrium absorption of H_2S is not affected by particle sizes. These observations may suggest that the intraparticular mass transfer of H_2S into pores of the sorbent is a limiting step for absorption of H_2S into the sorbent at 350°C.

Reactivity of the TU-1 sorbent in the form of 1-mm cylindrical rods was compared with that of the ZT-4 sorbent at 350 °C,as shown in FIGURE 8. The TU-1 sorbent removes less H_2S than the ZT-4 sorbent,based on the experimental data generated from the 35-cm^3 batch reactor. This fact may suggest that reactivity of the TU-1 sorbent is poor in comparison with that of the ZT-4 sorbent.

FIGURE 9 illustrates durability of the TU-1 sorbent as well as the ZT-4 sorbent by weighing the spent sorbent after each experimental run. The batch reactor was shaken horizontally at 50 rpm to eliminate effects of transfer of H_2S from the bulk reaction gas mixture to the solid sorbent in the micro batch reactor. The weight gain of the ZT-4 sorbent increases with reaction duration below equilibrium absorption and decreases with reaction duration above equilibrium absorption. This fact may indicate that the ZT-4 sorbent particles in the batch reactor were abraded by shaking the batch reactor for an extended reaction duration.

The TU-1 sorbent lost its weight, although it absorbed significant H_2S, as shown in FIGURES 6 and 9. These data suggest that durability of the TU-1 sorbent is very poor in comparison with that of the ZT-4 sorbent.

CONCLUSIONS

The following conclusions are drawn with experimental data obtained from micro-batch reaction experiments. Absorption of H_2S into the 316 SS reactor wall increases with absorption duration above 400°C. At 350°C, however, absorption of H_2S into the 316 SS reactor wall does not take place significantly, and previously absorbed H_2S appears to be

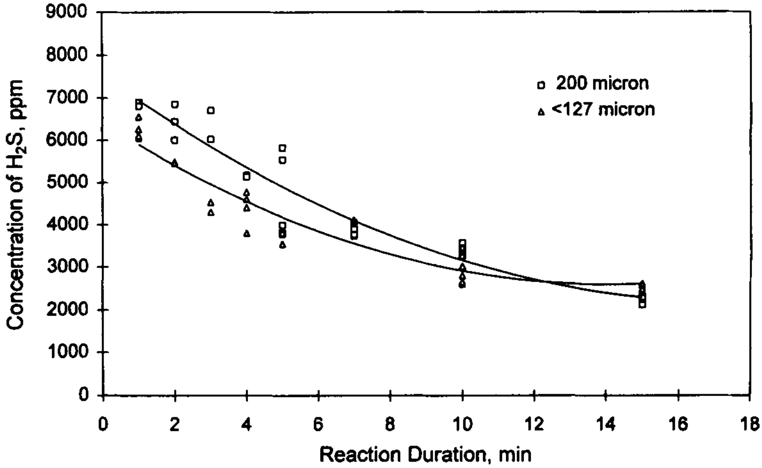

FIGURE 7. Effects of particle sizes on reactivity of 0.1 g ZT-4 sorbent with the initial concentration 9107 ppm H_2S in the presence of 0.085 g moisture at 350°C.

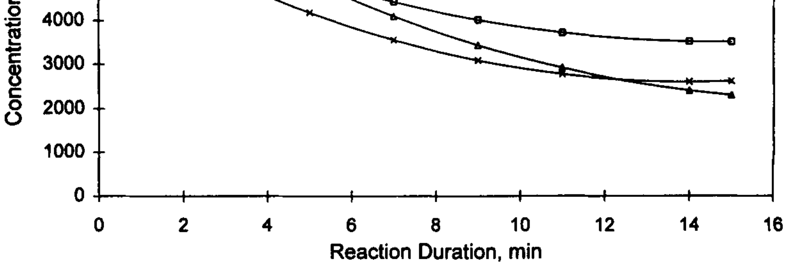

FIGURE 8. Reactivity of 0.1 g sorbent with the initial concentration 9107 ppm H_2S in the presence of 0.085 g moisture at 350°C.

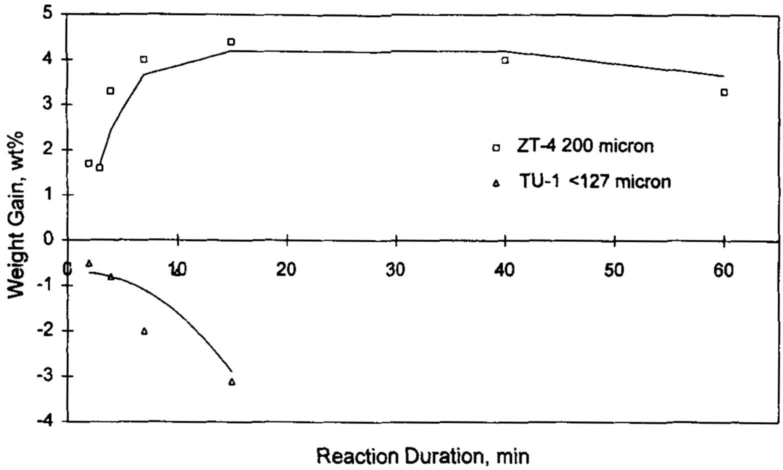

FIGURE 9. Durability of 0.1 g sorbent in the presence of initial 9107 ppm H_2S, initial 14.7-psia hydrogen, and 0.085 g moisture at 350°C.

released from the 316 SS wall. Reactivity of the sorbent increases with reaction temperatures.

Equilibrium absorption of H_2S into the 316 SS reactor wall increases with reaction temperatures. Increased moisture increases removal of H_2S below equilibrium absorption. This fact may indicate that moisture does not affect equilibrium absorption of H_2S into the ZT-4 sorbent at 350°C, but moisture affects dynamic absorption of H_2S into the ZT-4 sorbent at 350°C .

The minus-127-μm (micron) ZT-4 sorbent removes more H_2S than the 200- μm (micron) sorbent below equilibrium absorption. Equilibrium absorption of H_2S is not affected by particle sizes. These observations may suggest that the intraparticular mass transfer of H_2S into pores of the sorbent is a limiting step for absorption of H_2S into the sorbent at 350°C.

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