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Reactivity of Sorbents with Hot Hydrogen Sulfide in the Presence of Moisture and Hydrogen

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ABSTRACT

Hot-gas desulfurization for the integrated gasification combined cycle (IGCC) process has been investigated by many researchers to remove effectively hydrogen sulfide (H_2S) with various metal oxide sorbents at elevated temperatures. Various metal oxide sorbents are formulated with metal oxides such as Fe, Co, Zn, and Ti. In this article, reactivity of AHI-1 sorbent, obtained from the Research Triangle Institute (RTI), was investigated. Initial reactivity of AHI-1 sorbent with hydrogen sulfide was studied in the presence of various amounts of moisture and hydrogen at

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various reaction temperatures. AHI-1 sorbent consists of 20-w% Fe_2O_3, 10-w% ZnO, and 70-w% spent fluid cracking catalyst (FCC). The objectives of this research were to study initial reaction kinetics for the AHI-1 sorbent–hydrogen sulfide heterogeneous reaction system, to investigate effects of concentrations of hydrogen sulfide, hydrogen, and moisture on dynamic absorption of H_2S into the sorbent, to understand effects of space time of reaction gas mixtures on initial reaction kinetics of the sorbent–hydrogen sulfide system, and to evaluate effects of temperature and sorbent amounts on dynamic absorption of H_2S into the sorbent. Experimental data on initial reaction kinetics of hydrogen sulfide with the metal oxide sorbent were obtained with a 0.83-cm^3 differential reactor. The sorbent in the form of 130-μm particles was reacted with 1000 to 4000 ppm hydrogen sulfide at 450 to 600°C. The range of space time of reaction gas mixtures is 0.03 to 0.09 s. The range of reaction duration is 4 to 14,400 s.

Key Words: Metal oxide sorbents; Surface reaction; Intraparticle diffusion; Hydrogen sulfide; Coal gases; Gas clean-up; IGCC; Transport reactor; Gas-solid reaction.

INTRODUCTION

Coal is the most plentiful 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.[1–3]

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[4–8] 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.

EXPERIMENTAL SETUPS AND PROCEDURES

AHI-1 sorbent, obtained from Research Triangle Institute (Research Triangle Park, NC, USA), consists of 20-w% Fe_2O_3, 10-w% ZnO, and 70-w% spent fluid cracking catalyst (FCC). The spent fluid cracking catalyst, obtained from Rocky Mountain Salvage, Denver, Colorado, contains 0.51-w% Fe, 0.03-w% Zn, 317-ppmw Ni, and 471-ppmw V. Fe_2O_3 and ZnO are active ingredients and FCC is a support to impart attrition resistance. The attrition losses are 1.8 w% for 5 hour, and 3.8 w% for 20 hour, using a ASTM three-hole air jet attrition tester. The properties of the sorbent are shown in Table 1.

A 0.83-cm^3 micro differential reactor was used for experiments on absorption of H_2S into AHI-1 sorbent. The reactor contains typically 0.0058-cm^3 (0.01 g) sorbent. Under the typical absorption condition, the sorbent-particle bed in the reactor is fluidized.[9] Both conversion of H_2S in the fluidized bed reactor and change in concentration of H_2S in the fluidized bed are almost negligible, since the small amount of the sorbent was used in

Table 1. Properties of AHI-1 sorbent from the Research Triangle Institute (RTI).

BET area, m^2/g	110
Average pore diameter, Å	NA
Density, g/cm^3	1.7103
Pore volume, cm^3/g	0.162
Mean particle size, μm	130
Active ingredients	20-w% Fe_2O_3 10-w% ZnO

comparison with amount of H_2S fed into the reactor. Consequently, the concentration of H_2S throughout the fluidized bed reactor is almost same and approximately equal to the feed concentration. The surface reaction rate of H_2S with the sorbent is spatially uniform in the fluidized bed reactor during short initial absorption durations.

These RTI AHI-1 sorbent particles were reacted with simulated coal gases containing hydrogen sulfide in the 0.83 cm^3 titanium grade-2 micro differential reactor for 4 to 14,400 seconds at 450 to 600°C. Absorption amounts of hydrogen sulfide into the sorbent were analyzed with the LECO sulfur analyzer. The range of space (residence) time of the reaction gas mixture in the reactor was 0.03 to 0.09 s under the reaction conditions.

A differential reactor assembly mainly consists of four mass flow meters for gases, one differential reactor, one preheater, one high-pressure liquid pump for water, one four-way switch valve, one muffle furnace, three filters for gases, four check valves, and one water collection bottle (Fig. 1). The differential reactor was fabricated with one 5-cm-long, 1/4-inch titanium grade-2 tubing and two 1/4-inch external column end fittings. The preheater is made of 1/16″ Hastelloy C tubing.

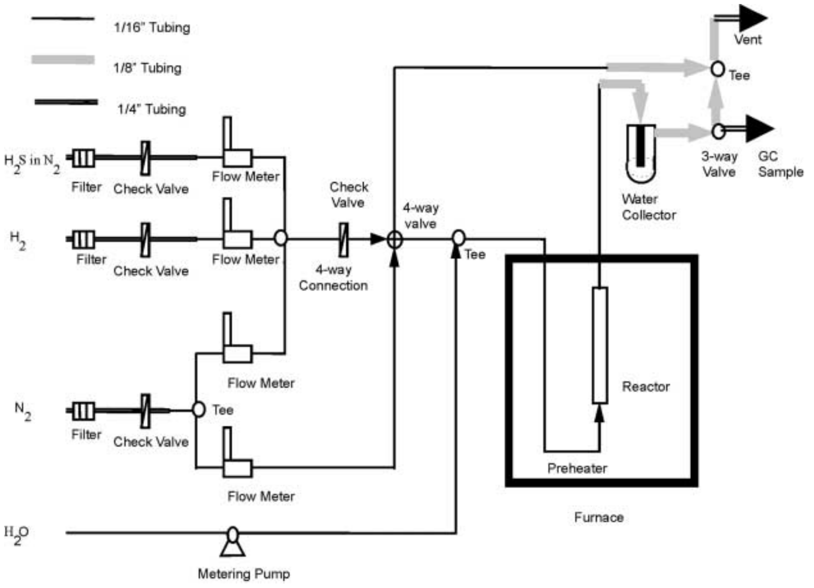

Figure 1. A differential reactor assembly.

Table 2. Experimental conditions for the reaction of AHI sorbent with hydrogen sulfide.

Reactor volume, cm^3	0.83
Temperature, °C	450–600
Reaction pressure, psia	18
Reaction time, s	4–14400
Space time under the absorption conditions, s	0.03–0.09
Mean particle size, μm	130
Amount of sorbent, g	0.005–0.05
Gas flow rate, cc/min at room temperature	250–750
Hydrogen, vol %	0–20
Moisture, vol %	0–20
Concentration of H_2S, ppm	1000–4000
Nitrogen, vol %	Remainder

The reactor was loaded with 130-μm sorbent particles. The reactor, loaded with the sorbent particles, was placed inside the muffle furnace to be heated at a desired temperature. Nitrogen was introduced into the sorbent-loaded reactor during preheating the reactor. When the temperature of the reactor reached the desired temperature, a simulated coal gas mixture, containing H_2S, was introduced into the reactor for a desired reaction duration, by switching nitrogen with the simulated coal gas mixture. The typical reaction conditions are shown in Table 2.

THEORY

Many researchers investigated absorption capacities of zinc titanate sorbents[10–13] and zinc ferrite sorbents.[9,14] An overall reaction equation for a gas–solid reaction of spherical particles[11,15] is described, using three reaction rate-controlling steps, such as mass transfer of gaseous reactants through gaseous reaction mixtures around solid reactants, intraparticle diffusion of gaseous reactants through porous reacted shells of solid reactants, and surface reaction of gaseous reactants with solid reactants (see eq. 1). Mass-transfer coefficient of H_2S through gaseous reaction mixtures, intraparticle diffusivity of H_2S through porous reacted sorbent shells, and surface reaction rate constant of H_2S reacted with a sorbent can be obtained with eq. 1, when the three rate-controlling steps are significant for overall absorption of H_2S into the sorbent. This equation is developed under the assumptions that the shrinking core model,[11] an elementary surface reaction,[6,7,11] and a quasi-steady state are valid.

Some researchers[5,12,13] applied the grain model to sulfidation data of zinc titanate sorbents, obtained from a thermo gravimetric analyzer (TGA). Their sulfidation experiments were conducted in stagnant gaseous reaction mixtures around sorbent particles for long sulfidation durations, while those in this study, were conducted in the fluidized differential reactor for short sulfidation durations.

$$\left(-\frac{d\left(\frac{r_C}{R}\right)}{dt}\right)^{-1} = \left(\frac{C_S R^2}{C_G}\right)\left(\frac{1}{Rk_g} - \frac{1}{\delta}\right)\left(\frac{r_C}{R}\right)^2 + \left(\frac{C_S R^2}{C_G \delta}\right)\left(\frac{r_C}{R}\right) + \left(\frac{C_S R}{C_G k_b'}\right) \quad (1)$$

Equation 2 is obtained by neglecting the mass transfer term of eq. 1. In other words, mass-transfer rates of gaseous reactants through gaseous reaction mixtures around solid reactants are much higher than both intraparticle diffusion rates of gaseous reactants through porous reacted shells of sorbent particles and surface reaction rates of gaseous reactants with reactive sites of sorbent particles for the development of eq. 2. Equation 2 is applied to the experimental data to obtain both intraparticle diffusivity values of H_2S through porous reacted shells of sorbent particles and surface reaction rate constants of H_2S with solid sorbent particles. The ratio of the radius of an unreacted core r_c to the radius of the sorbent R, r_c/R, is obtained with the conversion value of the sorbent, as shown in eq. 3.

Both the intraparticle-diffusion term and the mass-transfer term of eq. 1 are eliminated and the resulting equation is integrated in terms of reaction duration to obtain eq. 4, when surface reaction is a controlling step for absorption of gaseous reactants into a solid sorbent particle.

$$\left(-\frac{d\left(\frac{r_C}{R}\right)}{dt}\right)^{-1} = \left(\frac{C_S R^2}{C_G \delta}\right)\left(\frac{r_C}{R} - \left(\frac{r_C}{R}\right)^2\right) + \left(\frac{C_S R}{C_G k_b'}\right) \quad (2)$$

$$\left(\frac{r_C}{R}\right) = (1 - x_B)^{1/3} \quad (3)$$

$$t = \left(\frac{C_S R}{C_G k_b'}\right)(1 - (1 - x_B)^{1/3}) \quad (4)$$

where

r_c	radius of an unreacted core
δ	intraparticle diffusivity of a gaseous reactant
k_b'	reaction rate constant
k_g	mass-transfer coefficient of a gaseous reactant

R	radius of a spherical sorbent
t	reaction time
C_G	concentration of a gaseous reactant
C_S	molar concentration of a solid reactant
x_B	conversion of a solid reactant

Both surface reaction of a solid sorbent with H_2S and intraparticle diffusivity of H_2S through the porous reacted spherical shell of the solid sorbent are the dominant controlling steps for overall reaction of the solid sorbent with H_2S during initial reaction periods. Both surface reaction of H_2S with active sites of the metal oxide sorbent and intraparticle diffusivity of H_2S through the porous reacted shell of the sorbent initially control absorption of H_2S into the sorbent. However, absorption of H_2S into the porous sorbent is mostly controlled by intraparticle diffusivity of H_2S through the porous solid sorbent as reaction duration increases. The absorption equation, as shown in eq. 2, is developed assuming that the surface reaction, an elementary reaction,[6,7,16] occurs at the interface between the shrinking unreacted core and the reacted spherical shell of the solid sorbent after H_2S diffuses through the porous reacted spherical shell of the solid sorbent.

Surface reaction of H_2S with a solid sorbent also is justified to be an elementary reaction from the previous experimental data.[16] The surface reaction of H_2S with active sites of TU-24 sorbent in a batch reactor[16] was found to be first order, with respect to H_2S concentrations, and first order, with respect to sorbent amounts during short initial reaction durations. Several series of absorption experiments of H_2S with TU-24 sorbent in the presence of H_2S with various concentrations and the sorbent with various amounts were conducted in a batch reactor for the absorption duration of 60 s at 500°C.[16] An overall reaction rate equation for the reaction of H_2S with TU-24 sorbent in the batch reactor was developed with the experimental data, as shown in eq. 5. These data indicate that the initial surface reaction of the solid sorbent with H_2S at the interface between the unreacted core and the reacted shell of TU-24 sorbent particle be an elementary reaction. The fact that the surface reaction of H_2S with TU-24 sorbent is an elementary reaction is in agreement with previous works.[6,7,15,16]

$$r_A = k_A C_A{}^{\alpha} M_S{}^{\beta} = 19.29 C_A{}^{1.08} M_S{}^{1.04} \tag{5}$$

where

r_A	reaction rates of H_2S, g-mole/cm^3/s
C_A	concentrations of H_2S, g-mole/cm^3
M_S	quantities of sorbents, g/cm^3

k_A	reaction rate constant in terms of disappearance of H_2S, $cc^{(\alpha+\beta\ -\ 1)}/g^{\beta}/g\text{-mole}^{(\alpha-1)}/s$
α	reaction order with respect to concentrations of H_2S
β	reaction order with respect to quantities of sorbents
cc	cm^3

CALCULATIONS

Conversion of a sorbent, x_B, is calculated by dividing absorption of H_2S into the sorbent with the total absorption capacity of the sorbent. Ratios of the radius of an unreacted core r_c to the radius of the sorbent R, r_c/R, are obtained with conversion values of the sorbent (see eq. 3). Values of r_c/R are plotted against corresponding absorption durations and values of $(-d(r_c/R)/dt)^{-1}$ in the left-hand side of eq. 2 are obtained from slope values of this plotted curve at various corresponding absorption durations.

Values of $(-d(r_c/R)/dt)^{-1}$ as a dependent variable and values of $(r_c/R - (r_c/R)^2)$ as an independent variable (see eq. 2) are plotted and are applied to the linear least squares method to find both the value of the slope and the value of the intercept of this linear curve.

The value of the slope, obtained from the linear least squares method, is equal to the value of $C_SR^2/(C_G\delta)$, as shown in the first term of eq. 2. The value of intraparticle diffusivity δ can be computed by substituting the known value of the slope $C_SR^2/(C_G\delta)$ with the sorbent radius R, the H_2S concentration C_G, and the total absorption capacity of the sorbent C_S.

The value of the intercept, obtained from the linear least squares method, is equal to the value of $C_SR/(C_Gk_b')$, as shown in the second term of eq. 2. The value of surface reaction rate constant k_b' can be obtained by substituting the known value of the intercept $C_SR/(C_Gk_b')$ with the sorbent radius R, the H_2S concentration C_G, and the total absorption capacity of the sorbent C_S.

RESULTS AND DISCUSSION

Experiments on absorption of hydrogen sulfide into AHI-1 sorbent were carried out for 4 to 14,400 seconds at 450 to 600°C (see Table 2) to evaluate effects of concentrations of components in coal gases, such as H_2S, H_2, and those of reaction conditions, such as moisture, temperature, sorbent amounts, and space time on initial dynamic absorption of hydrogen sulfide into the sorbent. A typical simulated coal gas mixture consists of 4000-ppm hydrogen sulfide, 10 volume % moisture, 10 volume % hydrogen, and nitrogen as

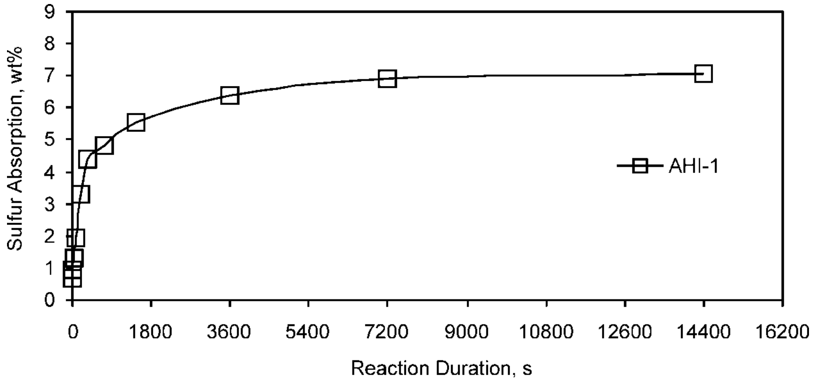

Figure 2. Effects of reaction duration on absorption of 4000-ppm H_2S on 0.01-g sorbent with 10-v% moisture and 10-v% hydrogen at 550°C and the space time 0.045 s.

remainder. A typical volumetric feed rate of a simulated coal gas mixture to the reactor was 500 cm^3/min at room temperature and atmospheric pressure. The temperature of the reactor was controlled in the furnace oven at 450 to 600°C. The pressure of the reactor was maintained at 18 psia. The total capacity of the sorbent for absorption of H_2S was determined with the experimental data shown in Fig. 2.

Effects of Temperature on Initial Dynamic Absorption of H_2S

Experiments on initial absorption of H_2S into AHI-1 sorbent were carried out for 4 to 360 seconds at 18 psia and in the reaction temperature range of 450 to 600°C to find effects of temperature on initial dynamic absorption of H_2S with AHI-1 sorbent. The concentrations of both moisture and hydrogen were maintained at 10 volume %. The concentration of hydrogen sulfide in the simulated coal gas mixture was maintained at 4000 ppm.

Initial absorption of H_2S into AHI-1 sorbent was affected by absorption temperature for short absorption duration of 4 to 60 seconds (see Fig. 3). Equation 2 was applied to the experimental data to obtain surface reaction rate constants as well as intraparticle diffusivity values of H_2S with the sorbent (see Fig. 4). The detailed procedure on calculating surface reaction rate constants of H_2S with active sites of the sorbent as well as intraparticle diffusivity values of H_2S through the porous reacted shell of the sorbent was discussed in the calculation section.

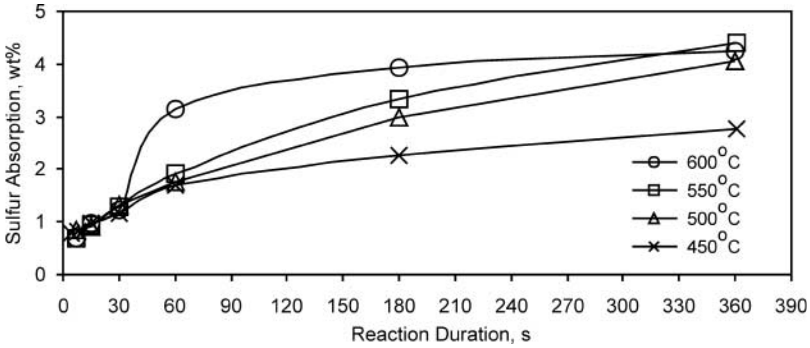

Figure 3. Effects of temperature on absorption of 4000-ppm H_2S on 0.01-g AHI-1 sorbent with 10-v% hydrogen and 10-v% moisture and the space time 0.045 s.

The range of surface reaction rate constants is 0.29 to 0.98 cm/s. The range of intraparticle diffusion values is 0.00011 to 0.00137 cm^2/s. Both surface reaction rate constants and intraparticle diffusivity values are affected by reaction temperatures (see Fig. 5). These observations indicate that reactivity of AHI-1 sorbent may be dependent on reaction temperature. These facts also suggest that the controlling steps for absorption of H_2S into sorbent particles are surface reaction of H_2S with reactive sites of sorbent particles and diffusion of H_2S through porous reacted shells of sorbent particles. Surface reaction rate constants decrease with increased reaction temperatures in

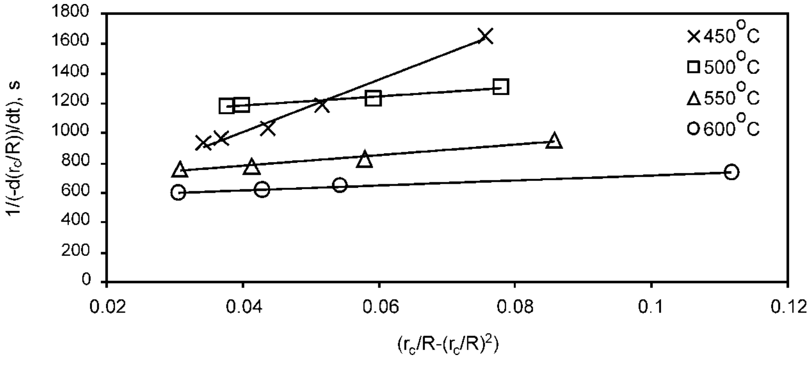

Figure 4. Effects of temperature on intraparticle diffusivity and reaction rate constant in the adsorption of 4000-ppm H_2S into 0.01-g AHI-1 sorbent with 10-v% H_2 and 10-v% moisture at the space time 0.045 s.

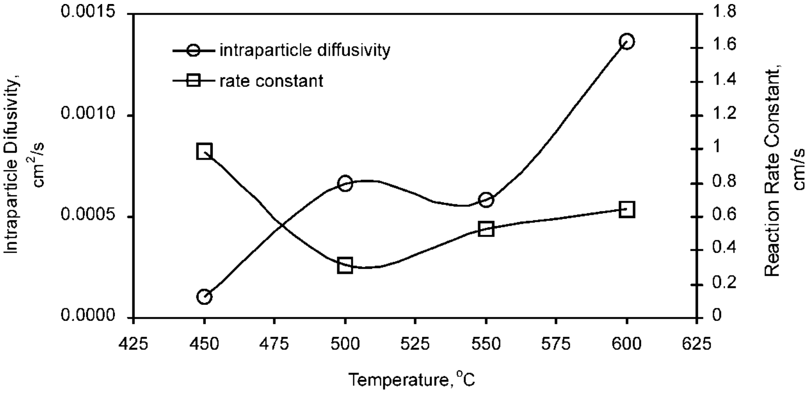

Figure 5. Effects of temperature on intraparticle diffusivity and reaction rate constant in the adsorption of 4000-ppm H_2S into 0.01-g AHI-1 sorbent with 10-v% H_2 and 10-v% moisture at the space time 0.045 s.

the reaction temperature range of 450 to 500°C, but surface reaction rate constants increase with reaction temperatures in the reaction temperature range of 500 to 600°C. These observations indicate that reactivity of the sorbent may decrease with increased reaction temperature over the temperature range of 450 to 500°C.

Effects of Moisture on Initial Dynamic Absorption of H_2S

Experiments on initial absorption of H_2S into AHI-1 sorbent were carried out for 4 to 360 seconds at 18 psia and 550°C to find the effects of moisture concentrations on initial dynamic absorption of H_2S with the sorbent. The concentrations of H_2S and hydrogen were maintained at 4000 ppm and 10 volume %, respectively. The concentration range of moisture in the simulated coal gas mixture was 0 to 20 volume %.

Initial absorption of H_2S into the sorbent is affected by concentrations of moisture for short absorption duration of 4 to 60 seconds (see Fig. 6). These facts may indicate that moisture is not inert for the reaction of AHI-1 sorbent with H_2S. Equation 2 was applied to the experimental data to obtain surface reaction rate constants and intraparticle diffusivity values of H_2S through the reacted shell of the sorbent (see Fig. 7). The range of surface reaction rate constants is 0.23 to 0.53 cm/s, and the range of intraparticle diffusivity values

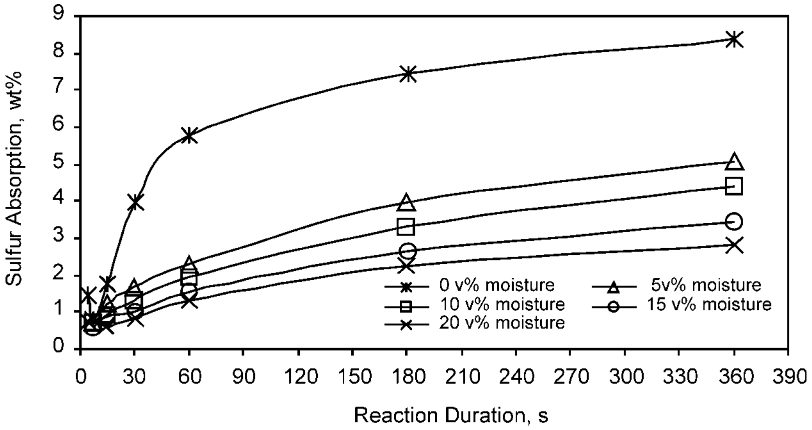

Figure 6. Effects of moisture on absorption of 4000-ppm H_2S on 0.01-g AHI-1 sorbent with 10-volume % hydrogen at 550°C and the space time 0.045 s.

is 0.00025 to 0.0015 cm^2/s (see Fig. 8). These observations indicate that reactivity of the sorbent and intraparticle diffusivity of H_2S through the reacted shell of the sorbent may decrease with increased moisture concentrations. These facts also suggest that the controlling steps for absorption of H_2S into sorbent particles are surface reaction of H_2S with reactive sites of sorbent particles and diffusion of H_2S through porous reacted shells of sorbent particles in the presence of moisture.

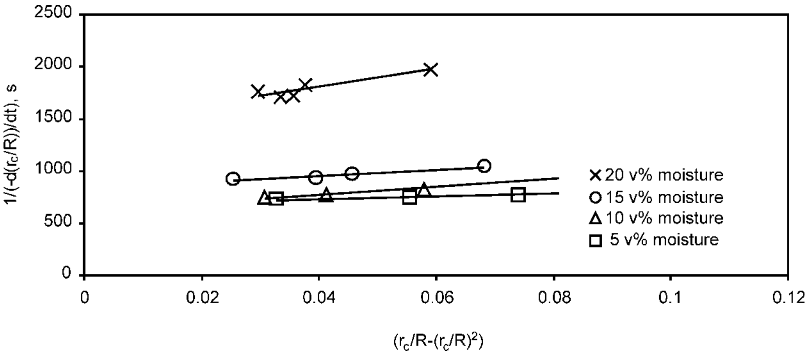

Figure 7. Effects of moisture on intraparticle diffusivity and reaction rate constant in the adsorption of 4000-ppm H_2S into 0.01-g AHI-1 sorbent with 10-v% H_2 and 10-v% moisture at 550°C and the space time 0.045 s.

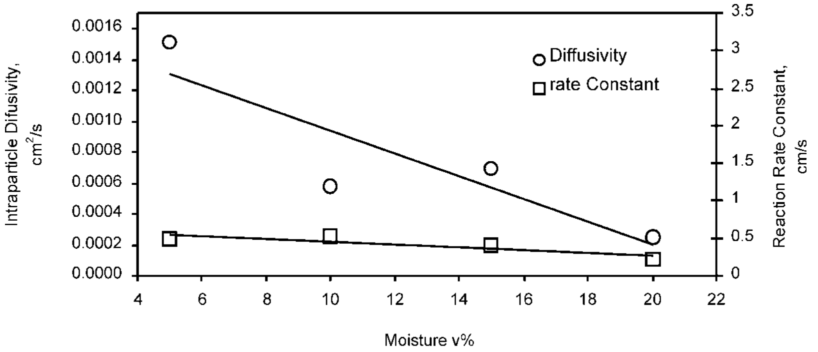

Figure 8. Effects of moisture on intraparticle diffusivity and reaction rate constant in the adsorption of 4000-ppm H_2S into 0.01-g AHI-1 sorbent with 10-v% H_2 and 10-v% moisture at 550°C and the space time 0.045 s.

Water is a product of sulfidation reactions of ZnO and Fe_2O_3. The initial rate of sulfidation may be affected by moisture, possibly due to inhibition caused by strong adsorption of water, thereby, blocking diffusion paths as well as active sites of reaction.[17]

A series of absorption reactions of H_2S into AHI-1 sorbent was carried out in the absence of moisture (see Fig. 6). Equation 4 was applied to the experimental data to obtain the surface reaction rate constant (see Fig. 9). The surface reaction rate constant is 2.05 cm/s in the absence of moisture. Initial absorption of H_2S into the sorbent in the presence of moisture is controlled by both the surface reaction step and the intraparticle diffusion step. However, initial absorption of H_2S into the sorbent in the absence of moisture is controlled by the surface reaction step only.

The total sulfur absorption capacity of the sorbent is 7.05 w% in the presence of moisture, whereas the total sulfur absorption capacity of the sorbent is 9.36 w% in the absence of moisture. These observations also suggest that moisture poisons reactive sites as well as diffusion paths of AHI-1 sorbent at the elevated temperature 550°C and affects mechanisms on absorption of H_2S into the sorbent.

Effects of Space Time on Initial Dynamic Absorption of H_2S

The absorption equation was developed under the assumption that mass-transfer rates of H_2S between gaseous reaction mixtures around a sorbent particle and the outside surface of the sorbent particle do not control

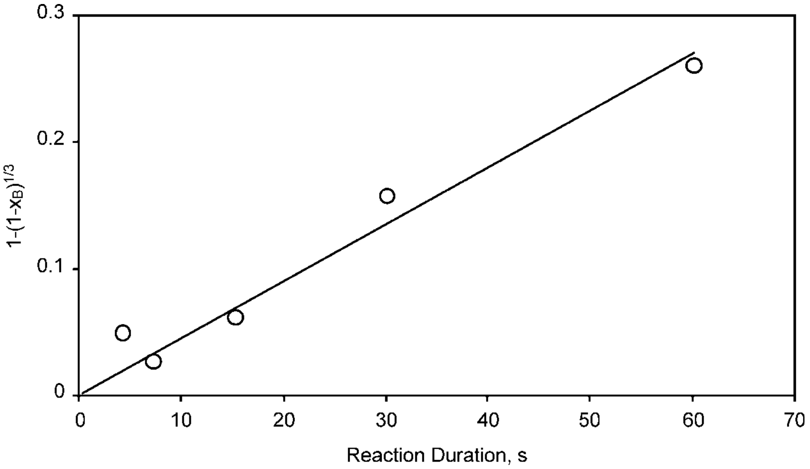

Figure 9. Absorption of 4000-ppm H_2S on 0.01-g AHI-1 sorbent with 10-volume % hydrogen in the absence of moisture at 550°C and the space time 0.045 s.

absorption of H_2S into the sorbent. Several series of experiments were conducted at various flow rates of gaseous reaction mixtures to examine validity of this assumption.

Eliminating the mass-transfer term of eq. 1 under the following assumption, develops the absorption equation (see eq. 2). Mass-transfer rates of H_2S through gaseous reaction mixtures around a sorbent particle are much higher than both intraparticle diffusion rates of H_2S through the porous reacted spherical shell and surface reaction rates of the sorbent particle with H_2S at the interface between the shrinking unreacted core and the reacted spherical shell of the sorbent particle, since the particle bed in the reactor is vigorously fluidized. Surface reaction rate constants of H_2S and intraparticle diffusion values, obtained from eq. 2, are expected to be independent of space times of reaction gas mixtures, since eq. 2 does not contain the space time term.

Experiments on the effects of space (residence) time on initial dynamic absorption of H_2S into the sorbent were conducted for the reaction duration of 4 to 360 seconds at 550°C and the space time of 0.03 to 0.09 s. The concentrations of both hydrogen and moisture were maintained at 10 volume %. The concentration of H_2S was maintained at 4000 ppm.

Space time does not significantly affect initial dynamic absorption of H_2S into AHI-1 sorbent in the space time range of 0.036 to 0.09 s (see Fig. 10).

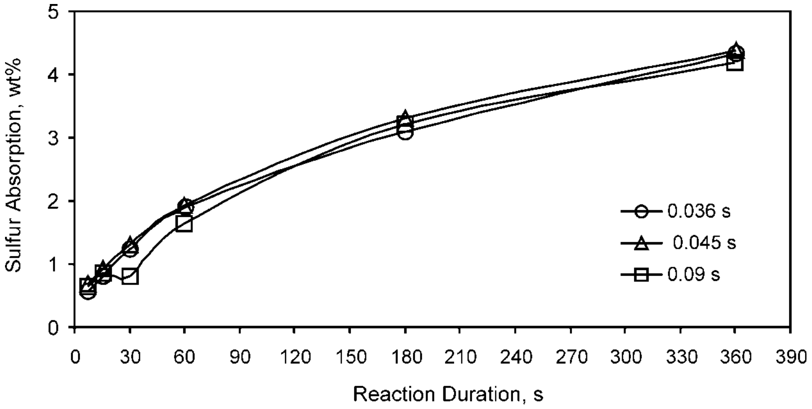

Figure 10. Effects of space time on absorption of 4000-ppm H_2S on 0.01-g AHI-1 sorbent with 10-v% hydrogen and 10 v% moisture at 550°C.

These observations suggest that the mass-transfer-controlling step of H_2S through the gaseous reaction mixture may be negligible for adsorption of H_2S into the sorbent in the space time range of 0.036 to 0.09 s.

Equation 2 was applied to the experimental data to obtain surface reaction rate constants and intraparticle diffusivity values of H_2S through the porous reacted shell of the sorbent (see Fig. 11). The detailed procedure on calculating surface reaction rate constants of H_2S with active sites of

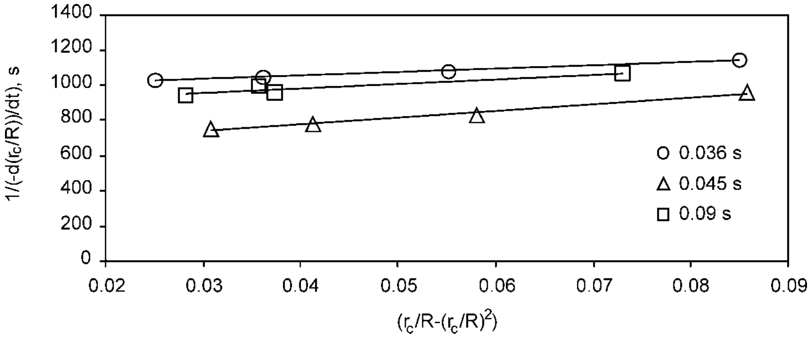

Figure 11. Effects of space time on intraparticle diffusivity and reaction rate constant in the adsorption of 4000-ppm H_2S into 0.01-g AHI-1 sorbent with 10-v% H_2 and 10-v% moisture at 550°C.

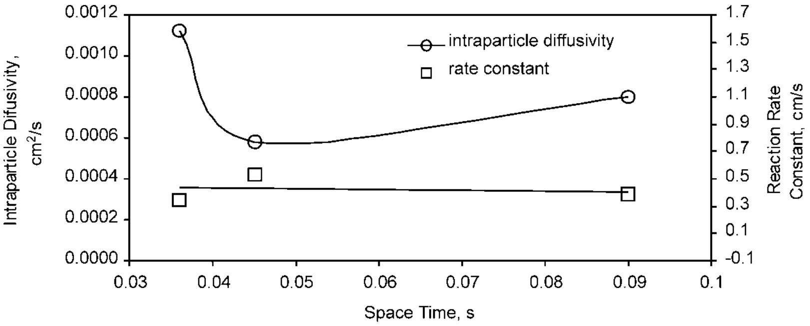

Figure 12. Effects of space time on intraparticle diffusivity and reaction rate constant in the adsorption of 4000-ppm H_2S into AHI-1 sorbent with 10-v% H_2 and 10-v% moisture at 550°C.

the sorbent as well as intraparticle diffusivity values of H_2S through the porous reacted shell of the sorbent was discussed in the calculation section.

The range of surface reaction rate constant is 0.34 to 0.53 cm/s, and the range of intraparticle diffusivity values is 0.0006 to 0.0011 cm^2/s (see Fig. 12). These observations indicate that reactivity of AHI-1 sorbent may be slightly affected by space time. These data also indicate that intraparticle diffusivity decreases with increased space time in the range of 0.036 to 0.045 seconds and is slightly affected by space time in the range of 0.045 to 0.09 seconds.

Effects of Concentration of H_2S on Initial Dynamic Absorption of H_2S

Experiments on the effects of concentration of H_2S on initial dynamic absorption of H_2S into AHI-1 sorbent were conducted for the reaction duration of 4 to 360 seconds at 550°C and the space time of 0.045 seconds. The concentrations of hydrogen and moisture were maintained at 10-volume %.

Concentrations of H_2S significantly affect initial dynamic absorption of H_2S into AHI-1 sorbent in the H_2S concentration range of 1000 to 4000 ppm (see Fig. 13). Equation 2 is not applicable at the H_2S concentration of 1000 to 2500 ppm. In this H_2S concentration range, differences between inlet concentrations of H_2S to the reactor and outlet concentrations of H_2S from the reactor are significant.

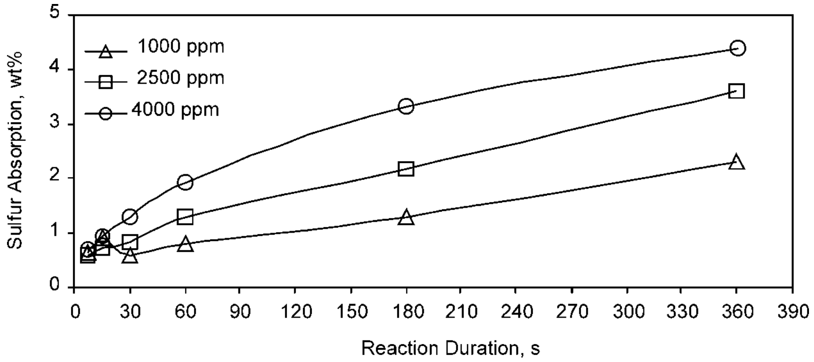

Figure 13. Effects of H_2S concentration on absorption of H_2S on 0.01-g AHI-1 sorbent with 10-v% hydrogen and 10-v% moisture at 550°C and the space time 0.045 s.

Effects of Sorbent Amounts on Initial Dynamic Absorption of H_2S

Experiments on the effects of sorbent amounts on initial dynamic absorption of H_2S into AHI-1 sorbent were conducted for the reaction duration of 4 to 360 seconds at 550°C and the space time of 0.045 seconds. The concentrations of both hydrogen and moisture were maintained at 10 volume %. The concentration of H_2S was maintained at 4000 ppm.

Amounts of AHI-1 sorbent slightly affect initial dynamic absorption of H_2S into the sorbent in the sorbent amount range of 0.01 to 0.05 g (see Fig. 14).

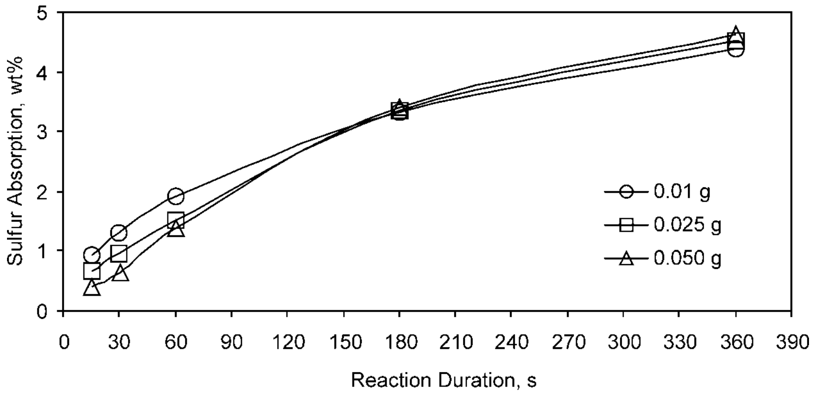

Figure 14. Effects of sorbent amount on absorption of 4000-ppm H_2S on AHI-1 sorbent with 10-v% hydrogen and 10-v% moisture at 550°C and the space time 0.045 s.

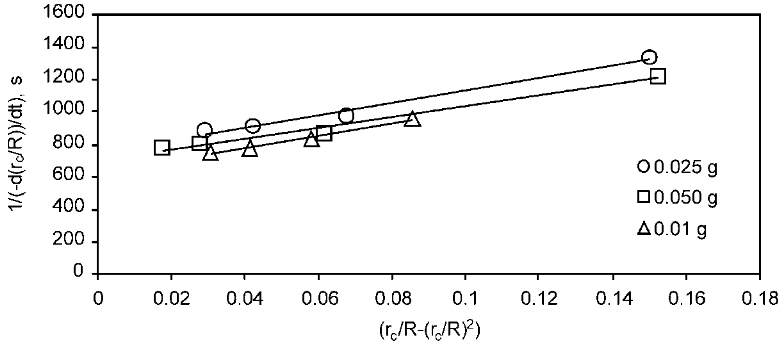

Figure 15. Effects of sorbent amount on intraparticle diffusivity and reaction rate constant in the adsorption of 4000-ppm H_2S into AHI-1 sorbent with 10-v% H_2 and 10-v% moisture at 550°C and the space time 0.045 s.

Absorption of H_2S decreases with increased amounts of the sorbent for the reaction duration 60 seconds, whereas absorption of H_2S appears to be independent of amounts of the sorbent after the reaction duration of 180 seconds (see Fig. 14). These observations suggest that surface reaction of the sorbent with H_2S may be a dominant controlling step for the initial reaction duration of 60 seconds, and diffusion of H_2S through the porous reacted shell of the sorbent is a dominant controlling step after the reaction duration of 180 seconds. Equation 2 was applied to the experimental data to obtain surface reaction rate constants and intraparticle diffusivity values of H_2S through the porous reacted shell of the sorbent particle (see Fig. 15). The detailed procedure on calculating surface reaction rate constants of H_2S with active sites of the sorbent as well as intraparticle diffusivity values of H_2S through the porous reacted shell of the sorbent was discussed in the calculation section.

The range of the surface reaction rate constant is 0.47 to 0.53 cm/s, and the range of the intraparticle diffusivity values is 0.00058 to 0.00066 cm^2/s. The surface reaction rate constants decrease slightly with increased sorbent amounts, and the intraparticle diffusivity values increase slightly with increased sorbent amounts (see Fig. 16).

Effects of Hydrogen Concentration on Initial Dynamic Absorption of H_2S

Experiments on the effects of hydrogen concentrations on initial dynamic absorption of H_2S into the sorbent were conducted for the reaction duration of

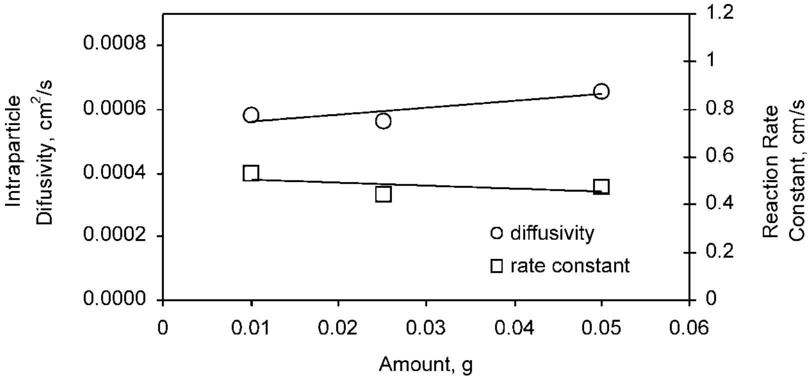

Figure 16. Effects of sorbent amount on intraparticle diffusivity and reaction rate constant in the adsorption of 4000-ppm H_2S into AHI-1 sorbent with 10-v% H_2 and 10-v% moisture at 550°C and the space time 0.045 s.

4 to 360 s at 550°C and the space time of 0.045 s. The concentration of moisture was maintained at 10-volume %. The concentration of H_2S was maintained at 4000 ppm.

Concentrations of hydrogen affect initial dynamic absorption of H_2S into AHI-1 sorbent in the hydrogen concentration range of 0 to 20 volume % (see Fig. 17). Effects of H_2 concentrations on absorption of H_2S into the sorbent are more pronounced with longer reaction durations. Equation 2 was applied to the experimental data to obtain initial surface reaction rate constants and

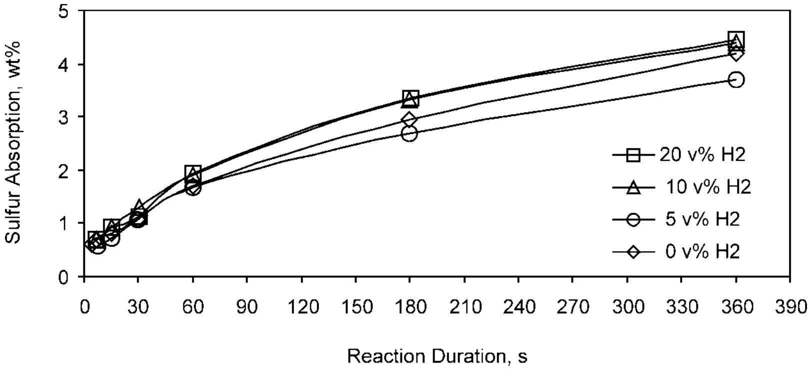

Figure 17. Effects of hydrogen on absorption of 4000-ppm H_2S on 0.01-g AHI-1 sorbent with 10-volume % moisture at 550°C and the space time 0.045 s.

intraparticle diffusivity values (see Fig. 18). The detailed procedure on calculating surface reaction rate constants of H_2S with active sites of the sorbent as well as intraparticle diffusivity values of H_2S through the porous reacted shell of the sorbent was discussed in the calculation section.

The range of the initial surface reaction rate constants is 0.29 to 0.53 cm/s, and the range of the intraparticle diffusivity values is 0.00058 to 0.00101 cm^2/s (see Fig. 19). Surface reaction rate constant increases with hydrogen concentration. Hydrogen is a reactant in the reaction of Fe_2O_3 to FeS ($Fe_2O_3 + 2H_2S + H_2 = 2FeS + 2H_2O$). Hydrogen also is needed to reduce the hematite (Fe_2O_3) to magnetite (Fe_3O_4) before the sulfidation reaction can proceed. Increased concentration of hydrogen increases the rate of reduction, which is a necessary step prior to sulfidation. This may explain why the overall sulfidation rate increases with H_2 concentration.[17]

These facts may indicate that hydrogen affects both surface reaction of H_2S with the sorbent and intraparticle diffusivity of H_2S through porous sorbents. Intraparticle diffusivity of hydrogen sulfide through the porous reacted shell of the sorbent decreases with increased hydrogen concentration in the hydrogen concentration range of 0 to 10 volume % (see Fig. 19). Intraparticle diffusivity of hydrogen sulfide through the porous reacted shell of the sorbent increases with increased hydrogen concentration in the hydrogen concentration range of 10 to 20 volume % (see Fig. 19). These observations may indicate that hydrogen itself changes pore structures of the reacted shell of the sorbent.

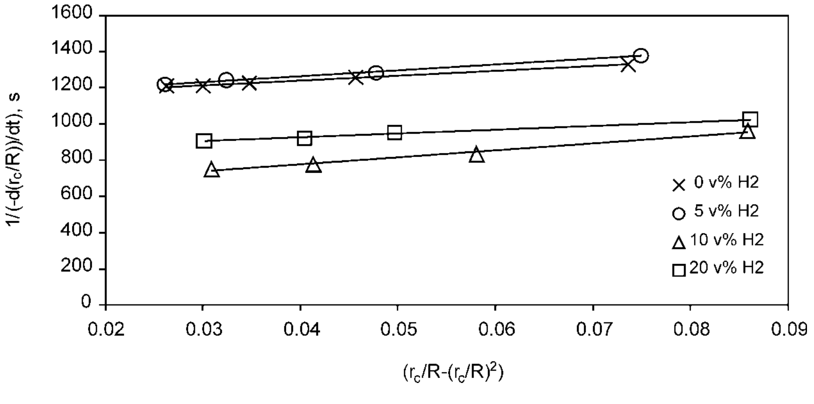

Figure 18. Effects of hydrogen on intraparticle diffusivity and reaction rate constant in the adsorption of 4000-ppm H_2S into AHI-1 sorbent with 10-v% moisture at 550°C and the space time 0.045 s.

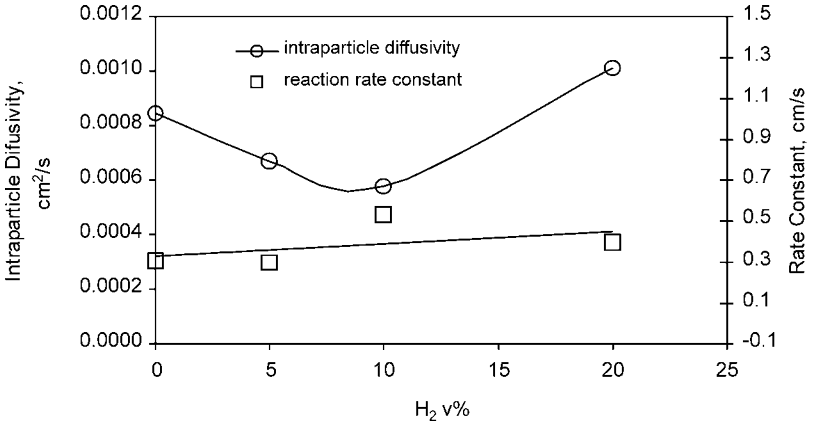

Figure 19. Effects of hydrogen on intraparticle diffusivity and reaction rate constant in the adsorption of 4000-ppm H_2S into AHI-1 sorbent with 10-v% moisture at 550°C and the space time 0.045 s.

CONCLUSION

The following conclusions were drawn, based on the experimental data generated from the micro differential reactor system, and their interpretations,

- Initial reactivity of AHI-1 sorbent is dependent on reaction temperature. The controlling steps for absorption of H_2S into AHI-1 sorbent particles are both surface reaction of H_2S with reactive sites of sorbent particles and diffusion of H_2S through porous reacted shells of sorbent particles.
- Both initial reactivity of AHI-1 sorbent with H_2S and intraparticle diffusivity of H_2S through the porous reacted shell of the sorbent decrease with increased moisture concentrations.
- Initial absorption of H_2S into AHI-1 sorbent in the presence of moisture is controlled by both surface reaction step and intraparticle diffusion step. However, initial absorption of H_2S into the sorbent in the absence of moisture is controlled by the surface reaction step only. The initial rate of sulfidation may be affected by moisture possibly due to inhibition caused by strong adsorption of water, thereby blocking diffusion paths as well as active sites of reaction.

- Hydrogen affects both surface reaction of H_2S with AHI-1 sorbent and intraparticle diffusivity of H_2S through the porous reacted shell of AHI-1 sorbent.

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REFERENCES

1. Andrus, H.E.; Thibeault, P.R.; Gibson, C.R. Combustion Engineering IGCC Repowering Project. Proceedings of the Twelfth Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting; Johnson, R.A., Jain, S.C., Eds.; 1992; Vol. I, p. 9.
2. Sears, R.E.; Griswold, G.H.; Frankhanel, M.O.; Kastner, C.E.; Pontius, D.H. Hot gas cleanup test facility for gasification and pressurized combustion. Proceedings of the Twelfth Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting; Johnson, R.A., Jain, S.C., Eds.; 1992; Vol. I, p. 53.
3. Virr, M.J. Toms Creek IGCC Demonstration Project. Proceedings of the Twelfth Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting; Johnson, R.A., Jain, S.C., Eds.; 1992; Vol. I, p. 42.
4. Sotirchos, S.V.; Yu, H.C. Overlapping grain models for gas–solid reactions with solid product. Ind. Eng. Chem. Res. **1988**, *27*, 836–845.
5. Lew, S.; Sarofim, A.F.; Stephanopoulos, M.F. Modeling of the sulfidation of zinc–titanium oxide sorbents with hydrogen sulfide. AIChE J. **1992**, *38* (8), 1161–1169.
6. Lew, S.; Sarofim, A.F.; Stephanopoulos, M.F. Sulfidation of zinc titanate and zinc oxide solids. Ind. Eng. Chem. Res. **1992**, *31*, 1890–1899.
7. Lew, S.; Sarofim, A.F.; Stephanopoulos, M.F. The reduction of zinc titanate and zinc oxide solids. Chem. Eng. Sci. **1992**, *47* (6), 1421–1431.
8. Lew, S.; Jothimurugesan, K.; Stephanopoulos, M.F. High-temperature H_2S removal from fuel gases by regenerable zinc oxide–titanium dioxide sorbents. Ind. Eng. Chem. Res. **1989**, *28*, 535–541.
9. Gupta, R.; Gangwal, S.K. Development of zinc ferrite sorbents for desulfurization of hot coal gas in a fluid-bed reactor. Energy Fuels **1992**, *6*, 21–27.

10. Woods, M.C.; Gangwal, S.K.; Jothimurugesan, K.; Harrison, D.P. Reaction between H_2S and zinc oxide–titanium oxide sorbents. 1. Single-pellet kinetic studies. Ind. Eng. Chem. Res. **1990**, *29*, 1160–1167.
11. Jothimurugesan, K.; Harrison, D.P. Reaction between H_2S and zinc oxide–titanium oxide sorbents. 2. Single-pellet sulfidation modeling. Ind. Eng. Chem. Res. **1990**, *29*, 1167–1172.
12. Ranade, D.P.; Harrison, D.P. The variable property grain model applied to the zinc oxide–hydrogen sulfide reaction. Chem. Eng. Sci. **1980**, *36*, 1079–1089.
13. Gibson, J.B., III; Harrison, D.P. The reaction between hydrogen sulfide and spherical pellets of zinc oxide. Ind. Eng. Chem. Process Des. Dev. **1980**, *19* (2), 231–237.
14. Gupta, R.P.; Gangwal, S.K. Enhanced durability of desulfurization sorbents for fluidized-bed applications. Proceedings of the Twelfth Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting; Johnson, R.A., Jain, S.C., Eds.; 1992; Vol. I, p. 240.
15. Levenspiel, O. *Chemical Reaction Engineering*, 3rd Ed.; John Wiley & Sons: New York, 1999.
16. Kwon, K.C.; Pallerla, S.; Roy, S.; Joincs, S.K.; Kumar, C. Reactivity of formulated metal oxide sorbents with hot hydrogen sulfide, Peer-Reviewed Proceedings of 11th Symposium. Sep. Sci. Technol. **2001**, *36* (5 & 6), 1375–1393.
17. Sasaoka, E. Chararterization of reaction between zinc oxide and hydrogen sulfide. Energy Fuels **1994**, *8*, 1100–1105.