OPTIMAL TEMPERATURE OF FIXED-BED REACTOR FOR HIGH TEMPERATURE REMOVAL OF HYDROGEN SULFIDE

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(Received 23 July 1991 • accepted 25 November 1991)

Abstract — To find optimal temperature of the reaction between H_2S gas and ZnO-5 at% Fe_2O_3 sorbent, the effluent gas from a fixed-bed reactor was analyzed by gas chromatography. The experimental results showed that H_2S removal efficiency of sorbent was maximum at 650℃ and EDX data were in accordance with this feature. XRD analysis exhibited intriguing phenomenon in that different mechanisms were observed at different temperatures. Chemisorption and chemical reaction was considered to be the main mechanism of H_2S removal at 600℃ and 650℃, respectively. SEM photographs supported this interesting phenomenon, but unfortunately TGA and DTA results could not distinguish it. To investigate the effect of sorbent deactivation on the reaction rate, deactivating factor was considered.

INTRODUCTION

Gas-solid reactions encompass a very broad field including the extraction of metals from their ores (iron oxide reduction, the roasting of sulfide ores, etc.), the combustion of solid fuels, coal gasification, and the incineration of solid refuse. The efficiency of coal gasification processes for producing gaseous fuels such as purification of coke oven gas using iron oxide [1, 2], desulfurization of ammonia synthetic gas [3], and gasification of residual oil [4] is deteriorated by major contaminants like SO_x, NO_x, and H_2S in the product gas stream. Especially control of hydrogen sulfide, which is very toxic, poisonous, corrosive and hazardous to a safe level, is essential. Although conventional process called cold scrubbing technique is effective for removal of H_2S, it has drawbacks due to loss of sensible heat of the gas. Recently it has been reported that mixed metal oxide sorbents enhance the efficiency of H_2S removal in hot coal-derived gas [5]. Although previous investigation for the desulfurization of H_2S using various metal oxide have been published [6-18], there wasn't optimization research for these gas-solid reaction yet.

In this present work, we want to obtain experimental parameter, especially temperature, and to investigate the temperature effect on the removal of H_2S

with the aids of our previous works [15-17].

EXPERIMENT

1. Preparation of Sorbent

Sorbent was prepared by a conventional method of synthesizing highly porous metal oxides [14]. According to this method, an aqueous solution containing the metal salts in desired proportion, and an organic polyfunctional acid with at least one hydroxy and one carboxylic function, was rapidly dehydrated under vacuum at about 70℃. The resulting amorphous solid foam was calcined at high temperature (usually 600-800℃) to form the mixed-oxide phase. The crystallized mixed oxides thus formed were homogeneous and highly porous.

The ferric oxide was added to prevent the vaporization of ZnO to elemental zinc, to increase the mechanical strength [18] and to accelerate the initial rate of ZnO sulfidation [15].

2. Characterization of Sorbent

The fresh and sulfided sorbents were characterized by several bulk and surface analysis techniques.

(1) X-ray diffraction (XRD) was performed for identification of crystalline phases in the mixed metal oxide sorbents.

(2) Scanning electron microscopy (SEM) combined with energy dispersive X-ray analysis (EDX) was used to observe the surface morphology, crystallite size, and

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Table 1. Physical properties of the fresh sorbent

Sorbent	ZnO-5 at% Fe$_2$O$_3$
Specific surface area	2.7 m^2/g
Average pore radius	12500Å
Average particle diameter	6-8×10^{-3} cm
Porosity	65%

Table 2. Experimental conditions of reaction

Temperature range	450-700℃
Gas composition	H$_2$S 2 vol%, N$_2$ 98 vol%
Total gas flow rate	200 ml/min
Pressure	1 atm

Table 3. Operating conditions for G.C.

Column material	Chromosil 310
Column length	8' ×1/8"
Carrier gas flow rate	N$_2$, 20 ml/min
Column temperature	50℃
Detector	TCD
Detector temperature	70℃
Current	75 mA
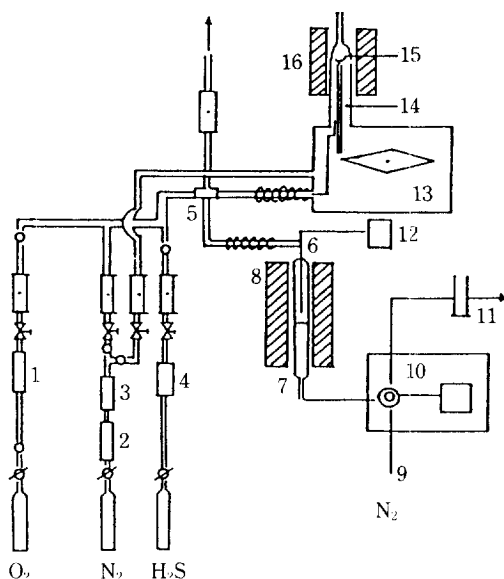
Fig. 1. Schematic diagram of experimental apparatus.

1. Zeolite trap	2. Zeolite trap
3. Purifier	4. Silica trap
5. Three-way valve	6. Thermocouple
7. Quartz reactor	8. Furnace
9. Carrier gas	10. G.C.
11. Soap flowmeter	12. Temperature-controller
13. T.G.A	14. Detector
15. Sample cell	16. Furnace

spatial variation of elemental distribution of the sorbents.

(3) Porosimeter was used to measure porosity, pore size distribution, particle size distribution, and specific surface area of the sorbents.

(4) Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were used to investigate the variation of property due to temperature.

The physical properties of fresh sorbent are listed in Table 1.

APPARATUS AND PROCEDURE

The reaction experiments were performed in the reactor system shown in Fig. 1. The reactor consisted

of a quartz tube, 1 cm i.d.×45 cm length, mounted vertically inside an electric furnace and instrumented with a Chromel-Alumel thermocouple moving inside a quartz thermowell (0.3 cm i.d.) concentric to the reactor. Different gases from regulated cylinders passed through purifiers and then through calibrated flow meters into a common gas line. The gas mixture then passed through the reactor in the downward direction and the lines leading to the reactor were heated. Temperatures at various locations in the reactor system were monitored by a thermocouple connected to a multichannel digital readout. The effluent gases exited through fixed-bed reactor were analyzed by a G.C. (Shimadzu GC-4C) equipped with a thermal conductivity detector and 8 ft×1/8 in. o.d. Chromosil 310 column operating at 50℃. Thermogravimetric analyzer (Shimadzu DT-30) was used to measure the weight changes of sorbent with temperature.

Table 2 and 3 represent the operating conditions of reactor system and G.C., respectively.

THEORETICAL BACKGROUND

In a widely accepted approach to the modeling of fixed-bed reactors, the solid particles and reacting gas are assumed to form a continuum, and the gross concentration and temperature profiles in the bed are consequently assumed to be smooth functions of axial and radial coordinates. Actually, however, three types of transport processes are involved in the operation of a fixed-bed reactor: (1) interparticle transport through the voids between the catalyst pellets (i.e., in the external field); (2) intraparticle transport within the catalyst pellet (i.e., in the internal field); and (3) interphase transport between the main stream of the fluid and surface of catalyst pellet.

The reaction model consists of a combination of models for all three transport processes. We adopt the quasi-homogeneous model of which intraparticle and interphase processes are unimportant and the concentration and temperature in the internal field are the same as those in the external field because of high porosity of our sorbent.

The model developed is based on the following assumptions and experimental conditions:

(1) The pseudo-steady state approximation is appropriate for describing the concentration of gaseous component.

(2) The reaction is irreversible.

(3) The external mass transfer resistance is negligible.

(4) The effective diffusivity is considered to be a constant.

(5) The reaction is the first order with respect to gas concentration.

(6) An isothermal condition and initial structure are maintained during the reaction.

According to the previous work by Levenspiel [23],

$$\frac{C_A}{C_{A0}} = 1 - X_A$$
$$= \frac{4 \cdot a \cdot \exp(Pe/2)}{(1+a)^2 \cdot \exp(a \cdot Pe/2) - (1-a)^2 \cdot \exp(-a \cdot Pe/2)}$$

where $Pe = U \cdot L/D$, $a = \sqrt{1 + 4 \cdot k \cdot t \ (1/Pe)}$

RESULTS AND DISCUSSION

Fig. 2 represents the typical reaction extent curve of fixed-bed reactor experiment. We adopt the value m from the most linear part of time vs. conversion curve instead of reaction rate constant k for the modeling of our fixed-bed reactor experiment because of the difficulty of obtaining the exact k value and obtain the value D from previous work [16]. The reaction rates of sorbents reacted with H_2S at various temperatures are depicted in Fig. 3. At 450°C, for 2 minutes, conversion is about 0.8. But the drastic decrease of conversion begins to occur after 5 minutes. Thus it is considered that this reaction temperature is so low that chemical reaction or chemisorption is can not occurred significantly. At 650°C, the sorbent removes H_2-S gas completely for about 50 min, and then gradual deterioration of H_2S removal efficiency of sorbent is occurred. After about 125 min, sorbent can't remove H_2S gas in the entering gas, that is, the amount of H_2S gas within effluent gas is equal to that within entering gas. The time taken for sorbent to lose H_2S removal capacity completely is defined as lifetime. Lifetimes of the sorbent at various reaction tempera-
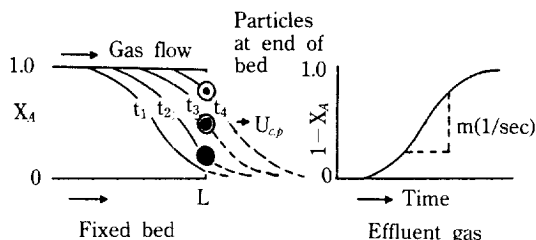
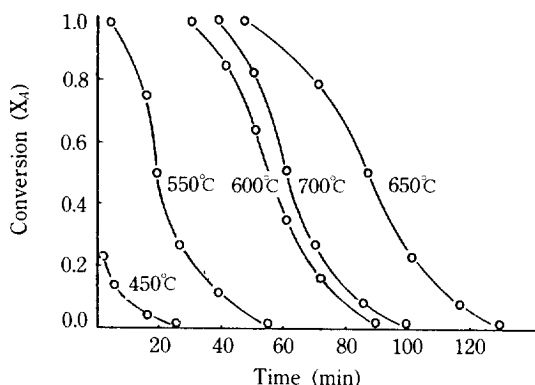

Fig. 2. Steady-state reaction rate in fixed-bed reactor.

Fig. 3. Conversion of H_2S vs. time at various temperatures with 1 g packing amount.

tures are shown in Fig. 4. At 650°C, the lifetime is about 125 min. So this temperature may be the optimal temperature of fixed-bed reactor.

Fig. 5 shows the comparison of reaction extent between experimental and theoretical values at 650°C. Theoretical values are obtained from the quasi-homogeneous model explained at previous section. After 80 min, deviation due to deactivation of the sorbent is observed. Deactivation of sorbent is considered to be caused by the chemisorption of produced oxygen on the Zn surface, the active site for H_2S removal. The chemisorption of oxygen on Zn surface was reported by King and Woodruff [21].

The effect of sorbent deactivation on the reaction conversion is represented by the following equation;

$$X = C_d \cdot X(T_r)$$

where X is the theoretical reaction conversion.

X(T_r) is the experimental one at arbitrary reaction temperature, and C_d is deactivating factor.

When the change in the deactivating factor is much smaller than that of reaction temperature T_r, the deactivating factor can be considered as a quasi-constant rather than variable during the reaction. When the change in the deactivating factor is quite large, the
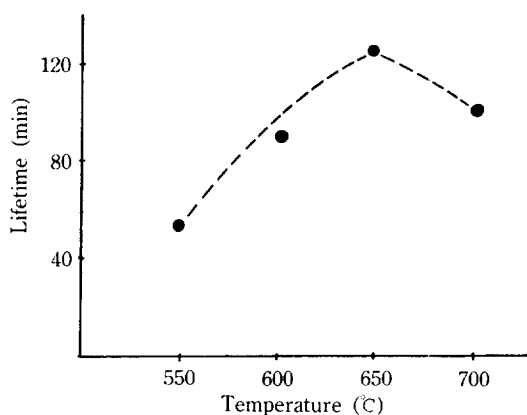
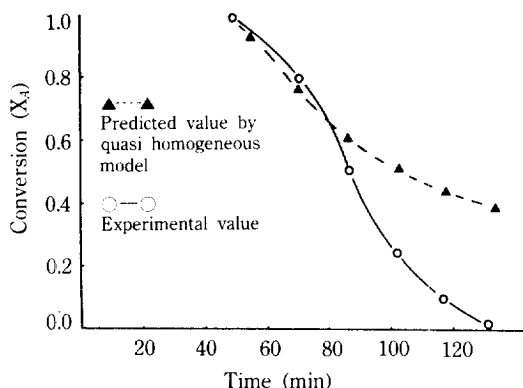Fig. 4. Lifetime vs. temperature of the reacted sorbent.

Fig. 5. Comparison between experimental and predicted
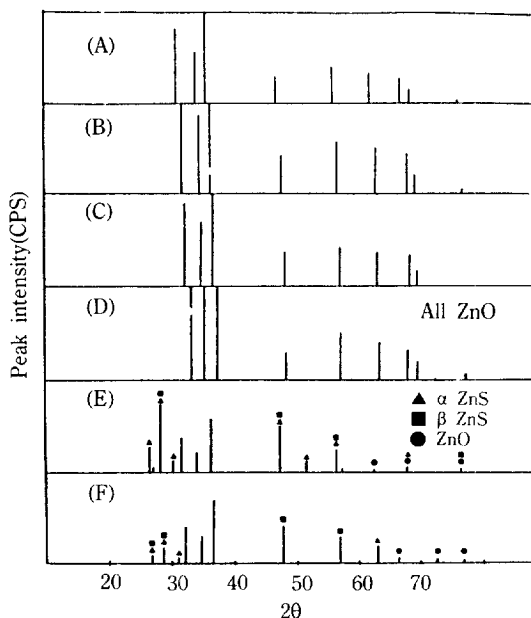values of the reacted sorbent at 650°C.

Fig. 6. X-ray diffraction pattern of reacted sorbent at var-
ious temperatures.
(A) fresh, (B) at 500°C, (C) at 550°C, (D) at 600°C,
(E) at 650°C, (F) at 700°C

deactivating factor must be considered as a variable
[18]. Unfortunately our approach to modify quasi-ho-
mogeneous model with the aid of deactivating factor
is failed because the temperature dependence on deac-
tivating factor isn't found out.

Fig. 6 shows XRD powder patterns of the reacted
sorbent at various reaction temperatures. Till 600°C,
there is no difference with respect to XRD pattern
of fresh sorbent except shifting of 2θ. This shifting
is considered to be caused by sintering of ZnO crystal
due to temperature increase. An interesting phenome-
non is observed at 600°C. From previous data, Fig. 3,
the removal of H₂S gas is confirmed. But XRD data
can detect ZnO crystal only. Thus the reaction mechan-
ism of sorbent with H₂S at this temperature is consid-
ered to be chemisorption. That is why we could not
simulate the experimental data at 600°C. The sulfida-
tion at 600°C is caused not by chemical reaction but
by chemisorption. Oudar and Wise [20] reported H₂S
chemisorption on ZnO surface. But they did not indi-

cate the definite reaction temperature. On the con-
trary, in case of 650°C, ZnS is detected only in XRD
pattern. Thus it is considered that chemical reaction
is the main mechanism. This result is in accordance
with SEM data. At 700°C, another interesting phenom-
enon that is, gradual decrease of Sphalerite (α-ZnS)
is observed. Although we can't find the way to detect
attacting oxygen, this is considered to be caused from
the reversible reaction between ZnS and product gas
oxygen, that is, the sulfidation reaction at 700°C is not
the first order with respect to H₂S concentration. The
chemisorption of oxygen on Zn surface was reported
by King and Woodruff [21]. Mutasher and Bowen
[22] suggested the possibility of reversibility be con-
sidered for fixed-bed reactor.

The SEM micrographs of the fresh and reacted one
are shown in Fig. 7. While the fresh sorbent and reac-
ted sorbent at 600°C have the similar morphological
feature, because of no effect of thermal sintering on
surface morphology, SEM photograph of the reacted
sorbent at 650°C is different, consisting of crystals due
to chemical reaction-induced "surface-roughing" [18].

The EDX data of the reacted sorbents are shown
in Fig. 8. For (B), the ratio of S to Zn is about 2 : 1,
while that of (A) is 1 : 2. Thus we conclude H₂S remov-
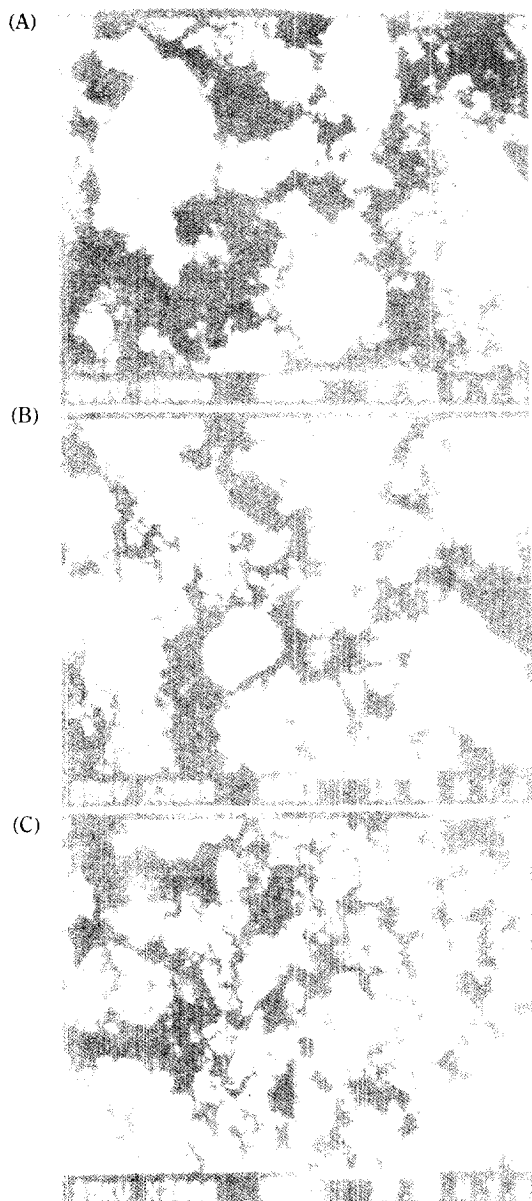al efficiency at 650°C is higher than that at 600°C by
two times approximately.

(A)

(B)

(C)

Fig. 7. Scanning electron microscopy of sorbent.
(A) fresh, (B) reacted at 600C, (C) reacted at 650
C

S 32.5%   Zn 65%
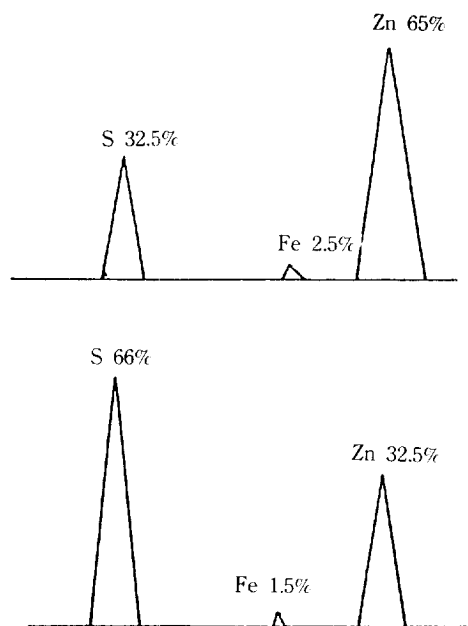
Fe 2.5%

S 66%

Zn 32.5%

Fe 1.5%

Fig. 8. Energy dispersive X-ray analysis.
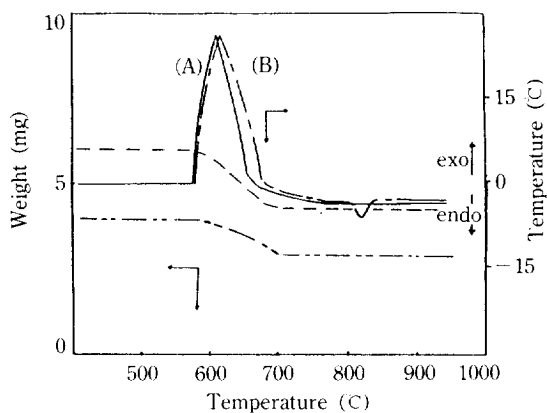(A) reacted sorbent at 600C
(B) reacted sorbent at 650C

Fig. 9. DTA and TGA curves of sulfided sorbents at 600
°C and 650°C.
(A) DTA curve at 600C, (B) DTA curve at 650C,
— — — TGA curve at 600C, — · · — TGA curve
at 650C

From TGA and DTA experiment of fresh sorbent to 1000C, no variation of properties is observed. Fig. 9 shows DTA and TGA curves of the sulfided sorbents at 600C and 650C. (A) and (B) have the same exothermic peaks due to oxidization of the formed sulfur at 600-700C. In case of (B), small endothermic peak is observed near 830C. Unfortunately we can't find out why this peak is appearred. TGA experiments

exhibit weight loss at the same temperature range. This weight loss corresponds to the decomposition of SO_2, and G.C. analysis conformed the production of SO_2. Although we can't elucidate difference between chemical reaction and chemisorption experimentally, it is meaningful to represent the possibility for the occurrence of this intriguing phenomenon from our

experiment. For the complete elucidation of different reaction mechanism at different temperature, more successive researches (ESCA, M.S analysis etc.) are required.

CONCLUSIONS

From the experimental results of the sulfidation in the fixed bed reactor, it was found out that H_2S removal efficiency is maximum at 650°C. Deviation from the quasi-homogeneous model was considered to be caused by the deactivation resulted from the chemisorption of the produced oxygen on the Zn surface, the active site for H_2S removal.

Furthermore, XRD analysis exhibited interesting phenomenon, that was, different mechanisms are observed at different temperature. It was considered that chemisorption and chemical reaction is the main mechanism of H_2S removal at 600°C and 650°C, respectively.

NOMENCLATURE

C_A : molar concentration of gaseous reactant [gmol/cm³]
C_{Ab} : molar concentration in bulk phase [gmol/cm³]
C_d : deactivating factor
D   : effective diffusivity [cm²/sec]
k   : reaction rate constant [sec⁻¹]
L   : length [cm]
m   : reaction rate constant defined in Fig. 2 [sec⁻¹]
Pe   : Peclet number
t   : time [sec]
U   : flow velocity [cm/sec]
U_{cp} : velocity of steady-state concentration profile
X_A : conversion of reactant gas
Z   : dimensionless length
2θ   : angle of X-ray diffraction [degree]

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