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KINETIC STUDY OF OXIDATION OF PELLETED ZINC SULFIDE POWDER HAVING GRAIN SIZE DISTRIBUTION

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Oxidation of porous zinc sulfide pellets, composed of fine grains having log-normal size distributions, was carried out using a differential flow reactor under oxygen partial pressure of 1-16 kPa and temperature of 953-1113 K.

The overall conversion rate data were represented by a simple power law rate expression. The reaction order with respect to the solid reactant varied with the standard deviation of the grain size distribution. This variation agreed well with the theoretical prediction by the grain model accounting for grain size distribution. The reaction order with respect to the gaseous reactant was 1/2.

The surface rate constant was then found to be correlated in an Arrhenius equation.

$$k' = 5.56 \times 10^8 e^{-244/RT} \quad (\text{mol}^{1/2}/\text{m}^{1/2} \cdot \text{s})$$

The rate constant agreed well with that for oxidation of sphalerite single crystals by other workers as well as with the rate constant reproduced from the data in the literature on oxidation of porous pelleted zinc sulfide.

Introduction

Gas-solid reactions involving a porous solid are numerous and industrially of great importance. For the interpretation and application of rate data observed in a variety of gas-solid reactions a number of kinetic models have been proposed.

It has been known that the kinetics by which the reaction proceeds depends entirely on the structure of the solid phase. The kinetic model describing the data is therefore required to reflect somehow the actual structure of the solid. In this light, the grain model^{16,18)} may be noteworthy for its simple but practical microscopic structural representation. This model assumes that the porous solid is an ensemble of grains of uniform size. A gaseous reactant diffuses through pores between grains and reacts on the unreacted core

formed in each grain.

The grain model is expected to be especially applicable when a pellet involved in the reaction is molded using powdered solid reactant by hand rolling, compression, sintering, etc. In the usual situation, however, the grains of the powdered reactant are considered not to be uniform in size but rather to have a size distribution. In such cases the model assuming uniform grain size may not be properly applied. Several workers^{1,10,15)} have predicted by numerical calculation the influence exerted upon the gross behavior by the grain size distribution. Although they pointed out the differences from the model assuming uniform grains, it was not very simple to apply their results to practical situations.

In this work the oxidation of pelletized zinc sulfide powder is investigated in detail. The rate data are analyzed on the basis of a simple rate equation derived from a grain model accounting for the grain

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size distribution,⁸⁾ and the rate constant is found to be correlated in an Arrhenius equation. The rate data in the literature are also subjected to interpretation by this kinetic model for comparison with the results of this work.

1. Experimental

1.1 Experimental apparatus and procedures

A differential reactor, a quartz tube of 10 mm inner diameter, was used to measure the rate of oxidation reaction. Oxygen concentration in the reactant gas was adjusted by controlling flow rates of air and inert nitrogen. The flow rate and oxygen content of the reactant gas were maintained at levels where both gas-film resistance and intraparticle temperature rise due to heat of reaction were negligibly small.

Pelleted sample of powdered zinc sulfide was sandwiched between quartz wool in the reactor tube and heated to a prescribed reaction temperature in a stream of inert nitrogen. The sample was then contacted with reactant gas by switching the streamlines connected to the reactor.

The progress of oxidation was followed by detecting SO₂ gas produced according to ^{2-4,6,14)}

The concentration of SO₂ in the effluent gas from the reactor was measured by an IR stream-line SO₂ analyzer.

The extent of conversion from zinc sulfide to zinc oxide was calculated by

$$\bar{X}_B = \frac{\text{cumulative amount of SO}_2 \text{ produced at any time}}{\text{total moles of SO}_2 \text{ produced by the end of reaction}}$$

The cumulative amount of SO₂ was determined by graphical integration of production rate curves of SO₂. The end of reaction was confirmed by detecting no SO₂ in the effluent gas. The total moles of product SO₂ gas obtained by graphical integration agreed well with the sulfur content of the sample within $\pm 1\%$ error.

1.2 Materials

1.2.1 Preparation of zinc sulfide pellets The original powdered zinc sulfide (99.9% crystalline ZnS: Mituwa Pure Chemicals) was screened once, using a 20 μm microsieve by way of precaution to remove peculiarly large grains. The powder was then screened at need by sets of microsieves to adjust the grain size in several ranks. For this purpose, combinations of microsieves of 5, 8, 10, 12.5, 15 μm were used.

The screened powder was blended with a small amount of ethanol to make a thick paste so that grains cohere, followed by the evaporation of ethanol at room temperature. The cake of solid obtained was cut into pellets of about 1 mm in size. The edges of

Fig. 1. SEM photograph of ZnS grains constituting sample pellets.

Fig. 2. Test of grain size distribution on log-normal probability chart.

pellets were rounded off by rolling in a mortar so that the pellets became spherical. Size of sample pellets was adjusted in the range 0.59–0.71 mm, for which size the intraparticle diffusion resistance was confirmed by preliminary experiments not to influence the oxidation rate in the temperature range investigated. For each oxidation run, about 10 sample pellets were used, being sandwiched in scattered fashion between quartz wool in the reactor tube.

Figure 1 shows a SEM photograph of a halved sample pellet prepared in the manner described above. The pellet is very porous, being composed of fine nonporous grains which are nearly spherical and nonuniform in size. There is neither sintering nor interconnection observed between grains.

1.2.2 Size distribution of powdered zinc sulfide

The size distribution of powdered zinc sulfide constituting sample pellets was measured by the phototransmission method. The cumulative weight fraction of grains greater than given size was observed by a centrifugal particle size analyzer (Shimadzu CP-50).

Figure 2 illustrates the distribution of the zinc sulfide powder on a log-normal probability chart, taking a few cases as examples. The cumulative

Table 1. Physical properties of zinc sulfide grains constituting sample pellets

Sample No. [—]	Mean grain diameter $2\bar{r}_g \times 10^6$ [m]	Standard deviation σ [—]
1	8.9	0.59
2	6.4	0.48
3	10.3	0.45
4	5.2	0.43
5	5.5	0.40
6	6.6	0.36
7	3.4	0.28
8	8.7	0.26
9	9.5	0.23

weight fractions of grains have linear relationships with grain size on this probability chart. The straight lines indicate that the zinc sulfide grains have a log-normal size distribution on the basis of weight, the density function of which is given by

$$g(r_g) = \frac{1}{\sqrt{2\pi}\sigma} \frac{1}{r_g} \exp \left[- \left(\ln \frac{r_g}{\bar{r}_g} \right)^2 / 2\sigma^2 \right] \quad (2)$$

The mean grain radius $\bar{r}_g$ and the standard deviation σ determined on the probability chart are shown for each sample in **Table 1**. The original grains have a widely spreading distribution while the screened grains have distributions in a narrower range.

2. Rate Equation by Grain Model with Size Distribution

The porous pellets used in this work are composed of fine spherical grains, which suggests that the grain model^{16,18)} is applicable. One may understand, however, that the grain model should be modified so that grain size distribution is taken into consideration.

Suppose that the following general gas-solid reaction is taking place in each individual grain forming an unreacted core.

When the resistance to product layer diffusion in each grain is negligible, the progress of reaction in the grain is represented by⁹⁾

$$\frac{t}{\tau} = 1 - (1 - X_B)^{1/3}; \quad 0 \leq t \leq \tau \quad (4)$$

where X_B signifies the extent of conversion of the grain at any time. The time required for complete conversion τ of a grain having radius r_g is given by^{7,9)}

$$\tau = \frac{r_g}{bk' C_A^n v_B} \quad (5)$$

where k' is the surface reaction rate constant and v_B is the molar volume of B. C_A is the concentration of A in

the environment surrounding the grain, and n is the reaction order with respect to the gaseous reactant.

When the resistance to diffusion through pores between grains in the pellet is also negligible, the concentration of A is uniform throughout the pellet. Then, using a density function $f(\tau)d\tau$, the overall conversion $\bar{X}_B$ of the pellet at any time is given by Eq. (4).

$$\bar{X}_B = 1 - \int_t^\infty \left(1 - \frac{t}{\tau} \right)^3 f(\tau) d\tau \quad (6)$$

In Eq. (6), $f(\tau)d\tau$ gives the weight fraction of grains which are completely converted in the time τ to $\tau + d\tau$.

The derivative of Eq. (6) with respect to t gives the overall conversion rate of the pellet, or

$$\frac{d\bar{X}_B}{dt} = 3 \int_t^\infty \frac{1}{\tau} \left(1 - \frac{t}{\tau} \right)^2 f(\tau) d\tau \quad (7)$$

Since the complete conversion time τ is linearly correlated to grain size r_g by Eq. (5), $g(r_g)$ is directly transformed into $f(\tau)$. Thus, with some manipulation, Eqs. (6) and (7) reduce to⁸⁾

$$\begin{aligned} \bar{X}_B = 1 - \frac{1}{\sqrt{2\pi}} \int_{\ln(t/\bar{\tau})/\sigma}^\infty \left(1 - \frac{t}{\bar{\tau}} e^{-\sigma\xi} \right)^3 \\ \times \exp \left[-\frac{\xi^2}{2} \right] d\xi \end{aligned} \quad (8)$$

$$\begin{aligned} \frac{d\bar{X}_B}{dt} = \frac{3e^{\sigma^2/2}}{\sqrt{2\pi}\bar{\tau}} \int_{\ln(t/\bar{\tau})/\sigma}^\infty \left(1 - \frac{t}{\bar{\tau}} e^{-\sigma\xi} \right)^2 \\ \times \exp \left[-\frac{(\sigma + \xi)^2}{2} \right] d\xi \end{aligned} \quad (9)$$

where ξ is defined by $\xi = \ln(\tau/\bar{\tau})/\sigma$ and $\bar{\tau}$ is the mean of the complete conversion time.

When plotting $d\bar{X}_B/dt$ against $1 - \bar{X}_B$ in log-log scale, both of which are calculated for a given value of σ by Eqs. (8) and (9), one may find that these two terms are approximated by a straight line for $\sigma \leq 1$.⁸⁾ Thus, in practical situations, one may correlate the overall conversion rate to the unconverted fraction by⁸⁾

$$\frac{d\bar{X}_B}{dt} = \left(\frac{d\bar{X}_B}{dt} \right)_{t=0} \cdot (1 - \bar{X}_B)^m \quad (10)$$

With the aid of Eqs. (5) and (9), the initial conversion rate is given by

$$\left(\frac{d\bar{X}_B}{dt} \right)_{t=0} = \frac{3bk' C_A^n v_B}{\bar{r}_g} \exp(\sigma^2/2) \quad (11)$$

where $\bar{r}_g$ is the mean grain radius.

Equation (10) provides a power law rate expression. The reaction order m with respect to the unconverted fraction $1 - \bar{X}_B$ of solid varies with the standard deviation σ of the grain size distribution, as shown by the solid line in **Fig. 3**.⁸⁾ When σ goes to 0,

Fig. 3. Reaction order m varying with standard deviation of grain size distribution.

that is, the size of grains is uniform, m becomes $2/3$. In this case, Eq. (10) reduces to the expression obtained by the ordinary grain model.

Equation (10) suggests that plotting $(d\bar{X}_B/dt)$ observed at any extent of conversion $\bar{X}_B$ against $1 - \bar{X}_B$ in log-log scale yields a straight line having a slope m . The intercept of the straight line at $\bar{X}_B=0$ gives the initial conversion rate $(d\bar{X}_B/dt)_{t=0}$, which allows one to evaluate the rate constant k' by Eq. (11).

3. Results and Analyses

3.1 Overall conversion rate

Graphical differentiation of the fractional conversion of zinc sulfide varying with time provides the reaction rate of oxidation at any extent of conversion. The rate of conversion so obtained is plotted against the unconverted fraction in log-log scale in Fig. 4. As suggested by Eq. (10), satisfactory linear relationships are obtained except for the very initial stage of reaction. The discrepancy during the initial stage, which was neglected in the present work, is considered to be due to the existence of induction time.

The results for No. 5 sample, obtained under different reaction temperatures and oxygen concentrations, suggest that, although the magnitudes of $d\bar{X}_B/dt$ are different correspondingly, the slopes of the straight lines are identical independently of these reaction conditions. Thus, the difference of slopes between different samples, that is, Nos. 1, 5 and 9, may be considered to result from the difference in properties of the grains constituting the sample pellets.

3.2 Test of data by the kinetic model

Extrapolating the conversion rate to $\bar{X}_B=0$ provides the initial conversion rate $(d\bar{X}_B/dt)_{t=0}$. The order of reaction with respect to gaseous reactant may be evaluated by plotting $(d\bar{X}_B/dt)_{t=0}$ observed at a fixed temperature against oxygen concentration C_A of the bulk reactant gas stream in log-log scale. Thus, Fig. 5 indicates by the slope of the straight line that the reaction order n yields $1/2$. This result agrees with that

Fig. 4. Conversion rate plotted against unconverted fraction of solid based on Eq. (10).

Fig. 5. Dependency of initial conversion rate on gaseous reactant concentrations.

Fig. 6. Test of whether data satisfies requirements from kinetics based on Eq. (11).

observed by Cannon and Denbigh.²⁾

In Fig. 6 the initial conversion rate divided by the square root of C_A is then plotted against $\exp[\sigma^2/2]/\bar{F}_g$, based on Eq. (11). This plot critically tests whether the rate data satisfy the requirement concerning the properties of grains predicted by the presently proposed kinetics. The proportionality for each reaction temperature confirms that Eq. (11) holds.

The order of reaction m with respect to solid

Table 2. Reaction order m obtained by slopes of straight line approximation based on Eq. (10)

Sample No.	Reaction temperature T [K]				Av. of m
	988	1019	1051	1083	
1	0.98	0.98–1.12	0.98	1.01–1.10	1.05
2	—	—	—	0.98–1.03	1.0
3	1.0	0.93	0.88	0.90–1.0	0.96
4	0.99	1.01	0.91	0.96	0.97
5	0.92	0.94	0.95	0.89–0.90	0.93
6	0.86	0.94	0.93	0.94	0.92
7	0.90	0.88	0.87	0.80	0.86
8	0.88–0.92	0.90	0.93	—	0.90
9	0.77	0.82	0.89	0.75–0.86	0.82

reactant may now be evaluated by the slopes of straight lines depicted in Fig. 4. The value of m evaluated for each sample is listed in Table 2. As already mentioned, the order m is dependent only on the kinds of sample used and is independent of reaction conditions. The values of m are plotted against the corresponding standard deviation σ of grains constituting pellets in Fig. 3. All the data agree well with the theoretical prediction depicted as a solid line in the figure. One may conclude from Figs. 3 and 6 that the oxidation of the present zinc sulfide pellets follows the reaction kinetics derived in the preceding chapter.

3.3 Rate constant

On confirming the kinetics, the surface rate constant may now be evaluated by observed initial conversion rate data on the basis of Eq. (11). Figure 7 illustrates the temperature dependency of the rate constant. This Arrhenius plot provides the activation energy of oxidation reaction as 244 kJ/mol. This value is very close to 252 kJ/mol observed by Ong *et al.*,¹²⁾ 210 kJ/mol by Cannon and Denbigh,²⁾ and 261 kJ/mol by Gerlach and Stichel.⁵⁾

Cannon and Denbigh²⁾ and Ong *et al.*¹²⁾ measured the oxidation rate of sphalerite single crystals of a few mm in size. They found that the reaction proceeded forming an unreacted core in the crystal in the regime of chemical reaction control. In the experiments by Cannon and Denbigh the rate of oxidation was also found to be proportional to the square root of the oxygen partial pressure. These facts strictly match the present kinetics although the size of crystals in which the reaction takes place is significantly different. The surface rate constant evaluated by Cannon and Denbigh is shown in Fig. 7 to be in good agreement with the present results. The rate constant reproduced from the data by Ong *et al.* by approximating $n=1/2$ also agrees fairly well with the present results.

The surface rate constant k' may be correlated in the temperature range 953–1113 K by

Fig. 7. Arrhenius plot of surface rate constant k' in comparison with results by other workers.

$$k' = 5.56 \times 10^8 e^{-244/RT} \quad (\text{mol}^{1/2}/\text{m}^{1/2} \cdot \text{s}) \quad (12)$$

4. Discussion

A number of experimental works on the oxidation of zinc sulfide have been carried out on single-particle systems, including both single crystals and grainy porous pellets. The rate data by individual workers are often compared on the basis of initial reaction rate per unit external surface area of the particle.^{4,6,11,14)} This comparison provides a significant difference in the data, especially showing the rate values for single crystals to be very much smaller than those for grainy porous pellets.

Since the reaction in nonporous single crystals was revealed to proceed on the reacting interface in the regime of chemical reaction control,^{2,12)} the reaction rate constant evaluated on this basis may be acceptable for single-crystal systems. However, in view of the zone-type reaction occurring in a porous particle,^{13,14)} the interfacial reaction model is not applicable to reacting grainy porous pellets. Thus, the rate values evaluated on the basis of external surface area may become extremely large due to the contribution of internal surface area in the reacting zone.

Limiting the situation in the regime where the conversion progresses under chemical reaction control, the reaction was often observed to proceed homogeneously throughout the pellet.^{3,17)} Takamura *et al.*¹⁷⁾ has shown that the oxidation reaction of grainy porous zinc sulfide pellets follows a rate equation represented by

$$\frac{d\bar{X}_B}{dt} = \left(\frac{d\bar{X}_B}{dt} \right)_{t=0} \cdot (1 - \bar{X}_B) \quad (13)$$

Equation (13) corresponds to a special case of Eq.

Fig. 8. Surface rate constant evaluated from literature data on oxidation of porous pelleted zinc sulfide.

(10) for $m=1$. Assuming that the zinc sulfide grains constituting their pellets also have the log-normal size distribution which most frequently applies,^{1,10,15)} the standard deviation may be estimated to be about 0.5 from Fig. 3. Thus, their data on the initial reaction rate may be subjected to analysis by Eq.(11) to evaluate the rate constant.

Since no information about grain radius is given in the literature, the rate constant may be evaluated in the following form.

$$\frac{k'}{\bar{r}_g} = \frac{e^{-\sigma^2/2}}{3bv_B C_A^n} \left(\frac{d\bar{X}_B}{dt} \right)_{t=0} \quad (14)$$

Figure 8 illustrates the rate constant reproduced with $\sigma=0.5$ and $n=0.5$ from the data by Takamura *et al.* In this figure the rate constant estimated from the data by Denbigh and Beveridge,³⁾ assuming the same values for σ and n , is also shown.

The straight portions at lower temperature, terminating at around 850 K, are considered to represent the chemical reaction control for the process. In the higher-temperature region the data seem to be influenced by diffusion limitation.

The rate constants by these workers are located close to the results of this work. The discrepancy between them is considered to be due to the differences in the properties of sulfides and also in the mean grain radius appearing in the denominator of the ordinate. The activation energies are evaluated to be 160 kJ/mol for the data by Takamura *et al.* and 230 kJ/mol by Denbigh and Beveridge, respectively. These values are not very different from the 244 kJ/mol obtained in this work.

It is already shown in Fig. 7 that the magnitude of the rate constant in this work agrees well with that for the oxidation of sphalerite single crystals. Therefore, the above interpretation reveals that the surface rate constants evaluated in the oxidation of porous pellets

do not differ very much from those of crystals but are of the same order of magnitude.

Conclusion

Oxidation of porous zinc sulfide pellets, composed of fine grains which are nonuniform in size, was carried out using a differential flow reactor. On confirming that the grain size of the zinc sulfide powder is log-normally distributed, the rate data were analyzed by the grain model accounting for grain size distribution.

The overall conversion rate was represented by a simple power law rate expression. The reaction order with respect to the solid reactant varied with the standard deviation of the grain size distribution. This variation was in good agreement with the theoretical prediction by the grain model accounting for grain size distribution. The reaction order with respect to the gaseous reactant yielded 1/2.

The surface rate constant was found to be correlated in an Arrhenius equation. The results obtained agreed well with those for the oxidation of sphalerite single crystals reported by other workers. The rate data in the literature on the oxidation of porous pelleted zinc sulfide were also subjected to interpretation by the present kinetic model. The surface rate constant reproduced from the literature data also agreed well in order of magnitude with the data from this work.

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Nomenclature

b	= stoichiometric coefficient	[—]
C_A	= gaseous reactant concentration	[mol/m ³]
E	= activation energy	[kJ/mol]
$f(\tau)$	= probability density function for complete conversion time represented by log-normal distribution	[—]
$g(r_g)$	= probability density function for grain radius represented by log-normal distribution	[—]
k'	= surface rate constant	[m ^{1/2} /mol ^{1/2} ·s]
m	= reaction order with respect to unconverted fraction of solid	[—]
n	= reaction order with respect to gaseous reactant	[—]
R	= ideal gas law constant	[kJ/mol·K]
r_g	= grain radius	[m]
$\bar{r}_g$	= mean grain radius	[m]
T	= absolute temperature	[K]
t	= reaction time	[s]
v_B	= molar volume of B	[m ³ /mol]
X_B	= extent of conversion of a grain	[—]
$\bar{X}_B$	= average extent of conversion of a pellet	[—]

ξ	= a parameter defined by $\xi = \ln(\tau/\bar{\tau})/\sigma$	[—]
σ	= standard deviation of grain size distribution	[—]
τ	= complete conversion time for a grain with radius r_g	[s]
$\bar{\tau}$	= mean of complete conversion time of grains	[s]

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HYDROLYSIS OF DIETHYL SUCCINATE CATALYZED BY CATION EXCHANGE RESIN

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Hydrolysis of diethyl succinate as a consecutive reaction was investigated in a batch slurry reactor catalysed by cation exchange resin.

Two models, one realistic and one simplified, were derived. The differences between the models were not significant under the conditions of this study, and both showed good agreement with experimental data.

The catalytic activities for gel-type resins were higher than for a macroreticular (MR)-type resin and a free acid. For gel-type resins, the reaction rate per equivalent increased as crosslinking decreased.

Introduction

Cation exchange resin of H^+ form has been used as acid catalyst for liquid-phase reaction and it has several advantages over free acid, such as easy separation from products. Since reactants, however, must reach active sites in the resin, the reaction rate may be influenced by particle size and crosslinking.

Many investigations have been made of the hydrolysis of ester catalyzed by cation exchange resin. The catalytic effectiveness factor was introduced to analyze intraparticle diffusion.^{14,15)}

Recently, a micro-macro pore model has been proposed for macroreticular resin catalyst.⁷⁾ It was

reported^{16,18)} that the activity of resin catalyst was greater than that of free-acid catalyst.

Although these studies were limited to simple reactions, many industrial reactions are complex and selectivity is an important factor along with catalyst activity. Theoretical studies of the catalytic effectiveness factor and selectivity for consecutive reactions have been made in terms of a single-pore model,^{19,20)} macro-micro pore model³⁾ and variable diffusivity model.²⁾ Experimental studies of common solid catalysts have been reported on the hydrogen of acetylene,¹⁰⁾ of mesityl oxide⁵⁾ and of phenylacetylene.⁹⁾

In this study, hydrolysis of diethyl succinate catalyzed by cation exchange resin of both gel and macroreticular (MR) types was investigated in a batch slurry reactor. Two models, one realistic and

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