Microkinetics of H$_2$S Removal by Zinc Oxide in the Presence of Moist Gas Atmosphere

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[Manuscript received February 25, 2003; revised March 16, 2003]

Abstract: The microkinetics of H$_2$S removal by ZnO desulfurization in H$_2$O-CO$_2$-N$_2$, H$_2$O-CO-N$_2$ and H$_2$O-O$_2$-N$_2$ gas mixtures was studied by thermogravimetric analysis. Experiments were carried out with 100–120 mesh ZnO powder at temperatures from 473 K to 563 K. The results show that the kinetic behaviors of desulfurization could all be described by an improved shrinking-core model. The activation energies of the reaction and the diffusion in different gas atmospheres were estimated.

Key words: kinetics, desulfurization, improved shrinking-core model, H$_2$S, zinc oxide

1. Introduction

Zinc oxide is known as a highly efficient desulfurizer of coal-derived fuel and chemical synthesis gases. Due to the high equilibrium constant for sulfitization [1,2], the use of ZnO leads to a very low concentration of hydrogen sulfide.

The reaction between ZnO and H$_2$S is a typical noncatalytic gas-solid reaction. Among the various models, the most frequently used is the unreacted shrinking-core model (SCM). This model assumes that the reaction occurs at a sharp interface that divides the reacted outer shell and the unreacted core of the solid and is mainly applied to highly nonporous solid reactants.

According to literature [3,4], SCM can be expressed as follows:

\[ t = AG_{tg}(x) + BP_{tg}(x) \]  

where

\[ A = \frac{\rho_{tm} \times r_{g0}}{k_s \times C_{A0} \mu} \]  

\[ B = \frac{\rho_{tm} \times r_{g0}^2}{6 \times D_{cg} \times C_{A0} \mu} \]

For spherical grain, $G_{tg}(x)$ and $P_{tg}(x)$ are defined as follows:

\[ G_{tg}(x) = 1 - (1 - x)^{\frac{3}{2}} \]  

\[ P_{tg}(x) = 1 - 3(1 - x)^{\frac{3}{2}} + 2(1 - x) \]

The relationship of $k_s$ and $D_{cg}$ vs. $T$ follows the Arrhenius equations:

\[ k_s = k_{s0} \times \exp \left( - \frac{E_a}{R_g T} \right) \]  

\[ D_{cg} = D_{cg0} \times \exp \left( - \frac{E_d}{R_g T} \right) \]

This solution reduced to the following solutions corresponding to pure chemical control (Equation 8) and pure diffusion control (Equation 9):

\[ t = AG_{tg}(x) \]  

\[ t = BP_{tg}(x) \]

The kinetics of H$_2$S or COS removal using ZnO or ZnO-MnO have been extensively studied in our laboratory using TG techniques. Considering that the ZnO powder sorbent used was in the form of
highly dense fine grains, which can be estimated as a non-porous solid, SCM was applied to describe the desulfurization kinetics. The microkinetics of H₂S removal by ZnO significantly deviated from the equations (Equation 1 and Equation 9) [5-7]. The linear plot of \( P_I(x)/G_I(x) \) versus \( t/G_I(x) \) expected by Equation 1 was not experimentally observed. In addition, in the region of diffusion control, a straight line relationship between \( P_I(x) \) and \( t \) was obtained which did not pass through the origin upon extrapolation. Therefore, SCM is limited for this reaction system, and the model was only applicable when the overall rate was controlled by the chemical reaction. In order to provide better fit with the experimental data, SCM was improved by the authors, and the kinetic characterization was carried out in regions of reaction and diffusion controlled rates. The improved shrinking-core model was more practical and facilitated, and it has been successfully used to approximate this reaction system [5-7].

The improved shrinking core model can be expressed as follows:

In the region controlled by the chemical reaction rate

\[
t = AG_I(x) \tag{10}
\]

In the region controlled by the diffusion rate

\[
t = B_1 + BP_I(x) \tag{11}
\]

\( B_1 \) is a correction term, with a unit of minutes, indicating the amount of time required to step into the diffusion-controlled region. For the reaction between ZnO and H₂S, the reaction order \( n \) is 1.

It should be noted that most of the previous investigations were performed in the absence of other gases except H₂S and N₂. However, in practical applications of desulfurization, there are varying amounts of H₂O, CO₂, CO, H₂ and O₂ in the coal-derived gas or synthesis gas. Thus the effects of these gases on the kinetics of the reaction between ZnO and H₂S must be studied. This paper focuses on the characterization of microkinetics of the reaction between ZnO and H₂S in H₂O-CO₂-N₂, H₂O-CO-N₂ and H₂O-O₂-N₂ gas mixtures using the improved SCM model.

\section{2. Experimental}

A commercially available zinc oxide sorbent supplied by West-South Chemical Engineering Research Institute was used in our experiments. The physical properties of the sorbent are given in Table 1. The specific surface area and pore volume were measured by a Micro-meritics Digisorb model 2,500 adsorption apparatus.

<table>
<thead>
<tr>
<th>( S_g/(\text{m}^2/\text{g}) )</th>
<th>( C_{\text{ZnO}}/% )</th>
<th>( \rho_{\text{cm}}/(\text{mol/L}) )</th>
<th>( V_g/(\text{ml/g}) )</th>
<th>( r_{\text{zo}}/\text{nm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>23.32</td>
<td>95.6</td>
<td>45.98</td>
<td>0.228</td>
<td>26.1</td>
</tr>
</tbody>
</table>

H₂S was generated by the reaction between FeS and hydrochloric acid. The reactive gas consisted of a certain amount of H₂S in N₂. H₂O, CO₂, CO or O₂ were added to change the gas atmosphere, and high-purity gases were used in all experiments.

A thermogravimetric analysis (TGA) apparatus was used to monitor weight changes in the sample. To prevent corrosion of the instrument by H₂S, the balance jar was constantly purged with nitrogen at a fixed flow rate. The reactive gas was introduced through one side arm. ZnO powder was uniformly spread on a circular pan hung from the sample arm of the microbalance (Sensitivity ±0.01 mg).

Conversion \( v/s. \) time curves were constructed from the thermogravimetric data by attributing the observed weight gain of the sorbent to the formation of zinc sulfide. The conversion of the sorbent can be calculated according to the following expression.

\[
x = \frac{\Delta W}{C_{\text{ZnO}} \times W} \times \frac{M_{\text{ZnO}}}{M_{\text{ZnS}} - M_{\text{ZnO}}} \tag{12}
\]

The experimental conditions are given in Table 2. The gas flow rate past the sample (800 ml/min) was high enough to minimize gas-phase mass-transfer resistance. The particle size of the sample was small enough to minimize the effects of pore diffusion.

<table>
<thead>
<tr>
<th>( T/\text{K} )</th>
<th>( C_{\text{ZnO}}/(\text{g/m}^2) )</th>
<th>( W/\text{mg} )</th>
<th>( \phi/\text{mesh} )</th>
<th>( C_{\text{H}_2\text{O}}/% )</th>
<th>( C_{\text{CO}_2}/% )</th>
<th>( C_{\text{CO}}/% )</th>
<th>( C_{\text{O}_2}/% )</th>
<th>( V/(\text{ml/min}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>473-563</td>
<td>12</td>
<td>10-12</td>
<td>100-120</td>
<td>5.39</td>
<td>15</td>
<td>5</td>
<td>0.4</td>
<td>800</td>
</tr>
</tbody>
</table>
3. Results and discussion

3.1. Influence of reaction temperature on kinetic parameters of desulfurization

The experiments were carried out at an H$_2$S concentration of 12 g/m$^3$ over a temperature range of 473–563 K in H$_2$O-CO$_2$-N$_2$, H$_2$O-CO-N$_2$ and H$_2$O-O$_2$-N$_2$ gas mixtures. Plots of conversion vs. time were obtained and are shown in Figure 1.

Figure 2 and Figure 3 depict the graphs of $G_{fg}(x)$ vs. $t$ and $P_{fg}(x)$ vs. $t$ from Figure 1. These figures indicate that the initial rate of H$_2$S removal was controlled by the surface reaction rate, and a linear relationship existed between $G_{fg}(x)$ and $t$. A deviation from the straight line occurred in the middle and last stages, suggesting that the reaction entered the diffusion rate-controlled region.

Figure 1. Influence of temperature on H$_2$S removal by ZnO in the different feed gases
Reaction conditions: reaction temperature (1) 473 K, (2) 503 K, (3) 533 K, (4) 563 K
feed gas (a) 12 g/m$^3$ H$_2$S, 5.39%H$_2$O, 15%CO$_2$, rest N$_2$; (b) 12 g/m$^3$ H$_2$S, 5.39%H$_2$O, 5%CO, rest N$_2$; (c) 12 g/m$^3$ H$_2$S, 5.39%H$_2$O, 0.4%O$_2$, rest N$_2$

Figure 2. Plot of $G_{fg}(x)$ versus time at different reaction temperatures
Reaction conditions: reaction temperature (1) 473 K, (2) 503 K, (3) 533 K, (4) 563 K
feed gas (a) 12 g/m$^3$ H$_2$S, 5.39%H$_2$O, 15%CO$_2$, rest N$_2$; (b) 12 g/m$^3$ H$_2$S, 5.39%H$_2$O, 5%CO, rest N$_2$; (c) 12 g/m$^3$ H$_2$S, 5.39%H$_2$O, 0.4%O$_2$, rest N$_2$
Figure 3. Plot of $P_{fg}(x)$ versus time at different reaction temperatures

Reaction conditions: reaction temperature (1) 473 K, (2) 503 K, (3) 533 K, (4) 563 K feed gas (a) 12 g/m$^3$ H$_2$S, 5.39%H$_2$O, 15%CO$_2$, rest N$_2$; (b) 12 g/m$^3$ H$_2$S, 5.39%H$_2$O, 5%CO, rest N$_2$; (c) 12 g/m$^3$ H$_2$S, 5.39%H$_2$O, 0.4%O$_2$, rest N$_2$.

The plots of $P_{fg}(x)$ vs. $t$ give a good linear relationship that does not pass through the origin over the experimental temperature range. It is clear that the improved SCM is favorable for describing the microkinetic behavior of H$_2$S removal by ZnO powder. For the diffusion-controlled stage, kinetic parameters $B_1$ and $B$ can be obtained according to Equation (11) as shown in Table 3.

Table 3. Kinetic parameters of $B$ and $B_1$ at different temperatures in the different feed gases

<table>
<thead>
<tr>
<th>$T/K$</th>
<th>5.39%H$_2$O + 15%CO$_2$ in feed gas</th>
<th>5.39%H$_2$O + 5%CO in feed gas</th>
<th>5.39%H$_2$O + 0.4%O$_2$ in feed gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>473</td>
<td>$B$ = 3225.8 $\times$ -85.87</td>
<td>$B$ = 2381.0 $\times$ -43.07</td>
<td>$B$ = 2040.8 $\times$ -13.86</td>
</tr>
<tr>
<td>503</td>
<td>$B_1$ = 1666.7 $\times$ -38.78</td>
<td>$B_1$ = 1063.8 $\times$ -14.39</td>
<td>$B_1$ = 990.1 $\times$ -12.86</td>
</tr>
<tr>
<td>533</td>
<td>$r$ = 819.7 $\times$ -17.80</td>
<td>$r$ = 793.7 $\times$ -15.39</td>
<td>$r$ = 757.8 $\times$ -8.82</td>
</tr>
<tr>
<td>563</td>
<td>$r$ = 342.5 $\times$ -7.02</td>
<td>$r$ = 333.3 $\times$ -19.48</td>
<td>$r$ = 552.5 $\times$ -15.18</td>
</tr>
</tbody>
</table>

3.2. Parameter evaluation

3.2.1. Determination of the reaction rate constant $k_s$ and activation energy

Due to very limited data in the chemical reaction stage, the initial reaction rate [5] was used to calculate the kinetic parameters in order to minimize the errors.

According to the literature [5], the initial reaction rate can be expressed as follows:

$$ \left( \frac{dx}{dt} \right)_{t=0} = \frac{3k_s \times C_{A0}}{\rho_{tm} \times r_{g0}} $$

Taking the logarithm gives

$$ \ln \left( \frac{dx}{dt} \right)_{t=0} = \ln \frac{3k_s \times C_{A0}}{\rho_{tm} \times r_{g0}} - \frac{E_a}{R_g T} $$

According to the Equation (14), reaction activation energy $E_a$ and the frequency factor $k_{so}$ can be obtained through the linear regression (Figure 4).
3.2.2. Determination of the diffusion coefficient

Taking the logarithm of Equation (3) gives:

\[
\ln \frac{1}{B} = \ln \frac{6D_{eq} \times C_{A0}}{\rho_{m} \times r_{g0}^2} - \frac{E_{d}}{RgT}
\]  

(15)

By linear regression, the diffusion activation energy \(E_{d}\) and frequency factor \(D_{eq0}\) can be estimated. The plots of \(\ln(1/B)\) vs. \(1/T\) are given in Figure 5, and Table 4 gives the kinetic parameters of \(\text{H}_2\text{~S}\) removal in the presence of moist gas atmosphere.

![Figure 5. Relationship of \(\ln(1/B)\) vs. \(1/T\)](image)

**Table 4. Kinetic parameters of \(\text{H}_2\text{~S}\) removal in the presence of moist gas atmosphere**

<table>
<thead>
<tr>
<th>Gas atmosphere</th>
<th>(E_a) (kJ/mol)</th>
<th>(k_{s0}) (mol/(cm(^2)·min))</th>
<th>(E_{d}) (kJ/mol)</th>
<th>(D_{eq0}) (mol/(cm·min))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2\text{~O}+\text{CO}_2)</td>
<td>11.48</td>
<td>4.91 \times 10^{-6}</td>
<td>54.60</td>
<td>1.84 \times 10^{-9}</td>
</tr>
<tr>
<td>(\text{H}_2\text{~O}+\text{CO})</td>
<td>31.79</td>
<td>5.10 \times 10^{-4}</td>
<td>45.55</td>
<td>2.74 \times 10^{-10}</td>
</tr>
<tr>
<td>(\text{H}_2\text{~O}+\text{O}_2)</td>
<td>18.78</td>
<td>2.93 \times 10^{-5}</td>
<td>31.20</td>
<td>1.49 \times 10^{-11}</td>
</tr>
</tbody>
</table>

3.3. A limitation of the study of the intrinsic kinetics in the reaction between ZnO and \(\text{H}_2\text{~S}\)

For the purpose of studying intrinsic kinetics, the authors wanted to carry out the experiments in the absence of intraparticle diffusion by minimizing particle size. However, previous research showed that it is very difficult to completely eliminate the effect of intraparticle diffusion because the process of \(\text{H}_2\text{~S}\) removal was characterized by the formation of a solid product, ZnS. Intraparticle diffusion included not only pore diffusion but also intragrain diffusion. In the absence of pore diffusion, the chemical reaction initially took place at the surface of the ZnO grain, and a product layer ZnS then formed on the exterior of the grain. The gaseous reactant \(\text{H}_2\text{~S}\) and products had to diffuse through this layer before the reaction could take place. This diffusion in the product layer was \(\text{S}^{2-}\) and \(\text{O}^{2-}\) diffusion in the solid grain, which cannot be eliminated by minimizing the particle size. This action only eliminates the effect of pore diffusion. Hence, the intrinsic rate constants can only be deduced at low conversions and limited reaction times.

3.4. A major characterization in the kinetics of removal \(\text{H}_2\text{~S}\) by ZnO

A curious observation in this study was that diffusion activation energy was higher than reaction energy, which agreed with our previous report [5–8]. The reason may be that the diffusion resistance of \(\text{S}^{2-}\) and \(\text{O}^{2-}\) in product layer played an important role, especially in the later stage. This intragrain diffusion (ion diffusion) needs to overcome a larger activation energy [2], which is usually more than the reaction energy [9]. This factor resulted in a higher activation energy for the diffusion-controlled period than for the surface reaction-controlled period.

3.5. Effect of gas atmosphere

As can be seen from the results, activation energy \(E_a\) and diffusion activation energy \(E_{d}\) varied in the presence of different gases, indicating that gas atmosphere had an effect on the reaction between ZnO and \(\text{H}_2\text{~S}\). The reason for this effect may be related to the performance of the ZnO surface in various atmospheres.

Because of the weak acidity of \(\text{H}_2\text{~S}\), the first step in the desulfurization should be the adsorption of \(\text{H}_2\text{~S}\) on the ZnO surface. So, the reaction rate between ZnO and \(\text{H}_2\text{~S}\) is related to the basicity of the ZnO surface. ZnO is a typical \(n\)-type semiconductor, and many of the performance characteristics of ZnO are connected with this trait, or we can say, with its surface electron concentration. Electron donating or accepting, which always occurs when gas is adsorbed on the ZnO surface [10], will directly affect the electron concentration and therefore the \(\text{H}_2\text{~S}\) adsorption as well. Otherwise, the hydroxylation of the surface, which might be raised by the adsorption of \(\text{H}_2\text{O}\), and the competitive adsorption of the acidic gases \(\text{CO}_2\) and \(\text{H}_2\text{~S}\) would all influence the performance of the ZnO surface.
4. Conclusions

1. The microkinetics of H₂S removal by ZnO in the presence of moisture gas atmosphere can be described using the improved shrinking core model.

2. The microkinetic parameters of desulfurization based on the improved shrinking core model were given.

Acknowledgements

The author would like to express gratitude to the National Key Fundamental Research Project of Science and Technology (973) (No.G1999022104-1) with their financial aid.

Notation

\( C_{A0} \) — concentration of gaseous reactant H₂S in bulk phase, g/m³
\( C_{H2O} \) — concentration of H₂O in bulk phase, vol %
\( C_{CO2} \) — concentration of CO₂ in bulk phase, vol %
\( C_{CO} \) — concentration of CO in bulk phase, vol %
\( C_{O2} \) — concentration of O₂ in bulk phase, vol %
\( C_{ZnO} \) — concentration of ZnO in grain, wt %
\( D_{eg} \) — diffusion coefficient, mol/(cm·min)
\( D_{eg0} \) — frequency factor, mol/(cm·min)
\( E_a \) — activation energy of chemical reaction, kJ/mol
\( E_d \) — activation energy of grain diffusion, kJ/mol
\( G_{fs}(x) \) — conversion function defined following Equation (4)
\( k_s \) — chemical reaction rate constant, mol/(cm²·min)
\( k_{s0} \) — frequency factor, mol/(cm²·min)
\( M_{ZnO} \) — molar mass of ZnS, g/mol
\( M_{ZnS} \) — molar mass of ZnS, g/mol
\( P_{fs}(x) \) — conversion function defined following Equation (5)
\( R_s \) — gaseous constant, 8.314 J/(mol·K)
\( r \) — correlation coefficient
\( r_{g0} \) — grain radium, nm
\( S_s \) — specific surface area, m²/g
\( T \) — reaction temperature, K
\( V_b \) — pore volume, ml/g
\( t \) — reaction time, min
\( W \) — sample weight, mg
\( \Delta W \) — change of sample weight, mg
\( V \) — total flow rate of reactant gas, ml/min
\( x \) — conversion, extent of reaction
\( \rho_{m} \) — ZnO concentration in grain, mol/L
\( \phi \) — particle size mesh

References