Sulfidation of Zinc Titanate and Zinc Oxide Solids

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The sulfidation of bulk mixed oxides of zinc and titanium of various compositions and Zn–Ti–O crystalline phases in H2S–H2–H2O–N2 gas mixtures was investigated in a thermogravimetric apparatus over the temperature range of 400–800 °C. Comparative sulfidation experiments with ZnO were also performed. In comparison to ZnO, the use of Zn–Ti–O solids allows raising the operating temperature for desulfurization of hot coal-derived fuel gas, e.g., by as much as 94 °C for solids with (Zn/Ti)atomic = 2/3. The initial sulfidation rate of Zn–Ti–O solids with (Zn/Ti)atomic ≤ 3 was approximately 1.5–2 times slower than for ZnO. Different zinc titanate phases (i.e., Zn2TiO4, ZnTiO3, and Zn2Ti3O8) had the same initial sulfidation rate. Similar activation energies (9–10 kcal/mol) were measured for ZnO and Zn–Ti–O sulfidation. No effect of H2 or H2O was observed on the initial sulfidation rate. However, at high conversions, rates were lower with increasing H2 concentrations. Fine particles and crystals were observed in sulfided ZnO as a result of ZnO reduction and subsequent vapor-phase reaction between Zn and H2S to form ZnS. These structural effects were largely absent in Zn–Ti–O solids.

Introduction

The removal of hydrogen sulfide (H2S) to sufficiently low levels from coal-derived fuel gases at elevated temperatures is crucial for the efficient and economic coal utilization in emerging advanced power generation systems such as the integrated gasification-combined cycle (IGCC) and the gasification–molten carbonate fuel cell (MCFC). For these technologies, highly efficient sulfur removal from several thousand parts per million (ppm) down to ~1 ppm for the MCFC or less than 100 ppm for the IGCC is needed. Commercial desulfurization processes are based on liquid scrubbing at or below ambient temperatures, resulting in considerable thermal efficiency loss as well as costly wastewater treatment.

Previous studies (Jalan and Wu, 1980; Grindley and Steinfeld, 1981; Flytzani-Stephanopoulos et al., 1985) have investigated the potential use of zinc oxide as a high-temperature regenerable sorbent. Kinetic studies using single pellets of zinc oxide were also performed (Gibson and Harrison, 1980; Ranade and Harrison, 1981). The thermodynamic equilibrium for sulfidation of ZnO is favorable, yielding desulfurization down to a few parts per million (ppm) H2S. Zinc sulfide can be regenerated if sufficiently high temperatures or low oxygen concentrations are used to avoid zinc sulfate formation. A major drawback of zinc oxide is that in the highly reducing atmosphere of coal-derived fuel gases, it is partially reduced to elemental zinc, which at high temperatures is volatile. Consequently, sorbent loss is observed at temperatures above 600 °C.

More recently mixed metal oxides have been studied in an effort to improve the properties of single oxide sulfur sorbents (Grindley and Steinfeld, 1983; Flytzani-Stephanopoulos et al., 1985). The mixed oxide sorbent zinc ferrite, ZnFe2O4, combining ZnO with Fe2O3 has been developed as an alternative to single zinc oxide sorbent (Grindley and Steinfeld, 1983) because of its high sulfur capacity, rapid reaction with H2S, and high H2S removal efficiency. Zinc ferrite decomposes into (ZnO + Fe3O4) in the reducing coal gas atmosphere. Hence, it is similarly limited (as ZnO) to an operating temperature of approximately 600 °C. Previous studies performed in this labo-
solids preparation by the citric acid complexation method using zinc acetate and titanium(IV) isopropoxide precursors followed by pyrolysis in air at different temperature conditions. The type of phases present depends on the Zn/Ti atomic ratio and the calcination temperature. The observed phase transformation with increasing temperature is $\text{Zn}_2\text{Ti}_3\text{O}_8 \rightarrow \text{Zn}_2\text{Ti}_2\text{O}_5 \rightarrow \text{Zn}_2\text{Ti}_4\text{O}_7$. At high calcination temperature ($\geq 1000^\circ\text{C}$), $\text{Zn}_2\text{Ti}_4\text{O}_7$ is the only stable mixed oxide phase for all $\text{Zn}-\text{Ti}-\text{O}$ solids, coexisting with either $\text{Zn}_2\text{O}_3$ or $\text{Ti}_2\text{O}_3$ phases depending on the solid stoichiometry ($\text{Zn}/\text{Ti}$ ratio). Also, $\text{Zn}_2\text{Ti}_4\text{O}_7$ is the stable phase for solids with $\text{Zn}/\text{Ti} \geq 2$ calcined at temperatures $\geq 700^\circ\text{C}$ for long periods of time ($\geq 12$ h). At temperatures below $800^\circ\text{C}$, all three zinc titanate phases may be present (Lew, 1990).

Table I shows the stoichiometry and XRD analysis of the various $\text{Zn}-\text{Ti}-\text{O}$ materials used in sulfidation experiments in this work. All sorbents were calcined at $720^\circ\text{C}$ for 12 h. The type of phases present depended on the $\text{Zn}/\text{Ti}$ ratio as shown graphically in Figure 1. Decreasing the $\text{Zn}/\text{Ti}$ ratio of the solids produced phases in the order $\text{ZnO} \rightarrow \text{Zn}_2\text{Ti}_2\text{O}_5 \rightarrow \text{Zn}_2\text{Ti}_2\text{O}_5 \rightarrow \text{Zn}_2\text{Ti}_4\text{O}_7$. There were some variations in the relative amounts of $\text{Zn}_2\text{Ti}_2\text{O}_5$ and $\text{Zn}_2\text{Ti}_4\text{O}_7$ as exemplified by the solids Z2T3-a and Z2T3-b in Table I, prepared, respectively, in flowing and static air calcination.

Effects of varying the Zn/Ti atomic ratio on the physical properties of the $\text{Zn}-\text{Ti}-\text{O}$ solids, i.e., surface area and pore volume, are shown in Figure 2. Solids with up to 50 mol % $\text{Ti}_2\text{O}_3$ are characterized by higher surface area and pore volume than $\text{ZnO}$ neat. Addition of small amounts of $\text{Ti}_2\text{O}_3$ to $\text{ZnO}$ has the largest effect, with a maximum in surface area and pore volume shown for ($\text{Zn}/\text{Ti})_{\text{atomic}} = 9/1$. These data indicate that $\text{Ti}_2\text{O}_3$ disperses $\text{ZnO}$ effectively preventing $\text{ZnO}$ particle growth (sintering). High levels of $\text{Ti}_2\text{O}_3$, however, and compound formation (e.g., $\text{Zn}_2\text{Ti}_2\text{O}_5$, $\text{Zn}_2\text{Ti}_4\text{O}_7$) reduce the overall surface area.

### Table I. Chemical Properties of Sorbents Used in Sulfidation Experiments

<table>
<thead>
<tr>
<th>sorbent</th>
<th>(Zn/Ti) (atomic ratio)</th>
<th>ZnO</th>
<th>$\text{Zn}_2\text{Ti}_2\text{O}_5$</th>
<th>$\text{Zn}_2\text{Ti}_4\text{O}_7$</th>
<th>$\text{Zn}_2\text{Ti}_4\text{O}_7$</th>
<th>$\text{Ti}_2\text{O}_3$ (rutile)</th>
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</thead>
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<tr>
<td>Z3T7</td>
<td>3/7</td>
<td>0</td>
<td>0</td>
<td>69</td>
<td>0</td>
<td>31</td>
</tr>
<tr>
<td>Z2T9-a</td>
<td>2/3</td>
<td>0</td>
<td>0</td>
<td>65</td>
<td>0</td>
<td>19</td>
</tr>
<tr>
<td>Z2T3-b</td>
<td>2/3</td>
<td>0</td>
<td>0</td>
<td>83</td>
<td>0</td>
<td>17</td>
</tr>
<tr>
<td>ZT</td>
<td>1/1</td>
<td>0</td>
<td>20</td>
<td>45</td>
<td>35</td>
<td>0</td>
</tr>
<tr>
<td>Z3T2</td>
<td>3/2</td>
<td>0</td>
<td>68</td>
<td>14</td>
<td>14</td>
<td>0</td>
</tr>
<tr>
<td>Z2T-a</td>
<td>2/1</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Z2T-b</td>
<td>2/1</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Z2T</td>
<td>3/2</td>
<td>28</td>
<td>72</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>ZnO</td>
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<td>0</td>
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<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*Prepared from zinc acetate and titanium(IV) isopropoxide with 1:1 mole ratio of metal ions to citric acid (unless otherwise noted). All solids calcined at 720°C for 12 h except for ZnO, which was calcined for 4 h. *Identified by X-ray diffraction. *Prepared with titanium tetrachloride. *Prepared with 1:2 mole ratio of metal ions to citric acid.
Figure 2. Effect of Zn-Ti-O composition on physical properties of the solid particles (90-125 μm): (a) surface area and (b) pore volume.

As a result of the preparation method, the sorbents are produced in a highly macroporous form. Table II shows the pore size distribution (based on Hg porosimetry) of Zn-Ti-O particles (90-125-μm size) after calcination in air at 720 °C for 12 h. Macropores (>1-μm diameter) typically comprise more than 70% of the pores. Such pore structures allow for kinetic studies in the absence of pore diffusion limitations even with relatively large particles (∼100 μm).

**Apparatus and Procedure.** Kinetic sulfidation experiments with solids containing various Zn/Ti atomic ratios were performed in a Cahn System 113-X thermogravimetric analyzer (TGA) equipped with a Cahn 2000 electrobalance, a Micron temperature controller, and a Bascom Turner data acquisition system. The TGA reactor system is shown in Figure 3. The TGA measured the weight gain as a function of the time required for Zn-Ti oxide sulfidation to ZnS and TiO₂. The solid was pretreated in a vacuum oven at 90 °C for 1 h to remove any absorbed H₂O before it was reacted in the TGA.

Gas flow rates were set by passing 6.3% H₂S-in-N₂, H₂, and N₂ gases through Brooks Model 5850E mass flow controllers. A gas flow rate of 350 cm³(STP)/min was used in the experiments. Approximately half the gas flow (containing H₂S, H₂, and N₂) entered the reactor (TGA) through the side arm. The other portion of the gas containing only N₂ entered the balance section of the TGA serving both to protect the balance from the corrosive H₂S and as a diluent to the reactant gas. Water vapor was added to the gas by bubbling nitrogen and hydrogen through a water saturator maintained at 25 °C in a three-neck flask assembly. The saturated gas stream was then mixed with the H₂S-in-N₂ gas and entered the apparatus side arm. A thin layer of sample (typically 1-3 mg of 90-125-μm-size particles) was placed in a hemispherical-shaped quartz pan suspended by a quartz hangdown wire. Isothermal sulfidation experiments were performed at temperatures between 400 and 800 °C. It was experimentally verified by varying the gas flow rate,
quantity of sample, and particle size that these experiments were performed in the absence of both mass transfer and pore diffusional limitations. Thus, the measured rate was due only to the intrinsic sulfidation kinetics and product layer diffusion. Typically, each sulfidation experiment was repeated at least once to verify reproducibility. In regeneration, the sulfided solids were reacted in 21% O₂–79% N₂ at 650 °C. Two cycles of sulfidation-regeneration were performed.

Results and Discussion

Initial Sulfidation Rate of Bulk Zn-Ti-O Sorbents. Initial rate experiments in the TGA were performed under isothermal conditions to determine the sulfidation reactivity of the solid listed in Table I. The results of these experiments at 600 and 700 °C in 2% H₂S–1% H₂–97% N₂ are shown in Figure 4. The initial rate was expressed in mmol of ZnS formed/cm²-s. The rate was normalized with the initial surface area of the sorbent. No bulk titanium sulfide was formed. The initial rate of sulfidation for ZnO at 600 and 700 °C was approximately 1.5–2 times higher than for all Zn-Ti-O sorbents containing ≥25 mol % Ti (based on Zn-Ti stoichiometry).

The initial sulfidation rate was similar for different zinc titanate phases despite the fact that sorbents with different Zn-Ti compositions formed different zinc titanate phases as shown in Table I. For example, a sorbent with 30 mol % ZnO–70 mol % TiO₂ contained a mixture of Zn₂TiO₄ and TiO₂, while a sorbent with 75 mol % ZnO–25 mol % TiO₂ was composed of Zn₂TiO₄ and ZnO. However, both of these sorbents had approximately the same initial sulfidation rates (Figure 4).

Since all Zn-Ti-O sorbents containing ≥25 mol % Ti (based on Zn-Ti stoichiometry) had approximately the same initial sulfidation rate, further kinetic experiments were performed with just two different types of Zn-Ti-O sorbents. Experiments were performed with ZT-a, a sorbent prepared with 2:1 atomic ratio of Zn:Ti, and ZT-a, which was prepared with 2:3 atomic ratio of Zn:Ti. Zn₂TiO₄ was the only crystalline phase identified by XRD in ZT-a, while ZT-a contained a mixture of Zn₂TiO₄, Zn₂Ti₃O₉, and TiO₂. For the purpose of comparison and in order to establish a base-line sulfidation performance level to meet, similar kinetic experiments were also performed with ZnO.

On the basis of SEM micrographs of the unreacted solids, the sorbents are composed of nonporous particles (or grains). In the absence of both diffusional and mass-transfer resistances, the irreversible surface chemical reaction can be described as

\[ R_0 = kC_{ZnS}^n \]  

where \( R_0 \) is the initial molar rate of ZnS formation per unit surface area of the solid reactant [mmol/(cm²-s)], \( k \) is the intrinsic rate constant, \( C_{ZnS} \) is the molar concentration of hydrogen sulfide [mmol/cm³], and \( n \) is the reaction order. The reaction orders (\( n \)) for ZnO and ZT-a sulfidations were both determined to be 1. Figure 5 illustrates the results obtained for ZnO and ZT-a sulfidations. The linearity of the variation in initial sulfidation rate with changing hydrogen sulfide concentration indicated a reaction order of 1. This agrees with the kinetic data reported by Westmoreland et al. (1977) for zinc oxide. Equation 4 was used to describe the initial sulfidation rate. As discussed in the previous section, the sulfidation experiments were performed in the absence of pore diffusional and mass-transfer resistances by using small particles and high gas flow rates. An Arrhenius relationship can be used to express the intrinsic rate constant as

\[ k = k_0 \exp[-E/RT] \]  

where \( k_0 \) is the Arrhenius frequency factor [cm/s], \( E \) is the activation energy [kcal/mol], \( R \) is the gas constant [1.987 × 10⁻³ kcal/(mol·K)], and \( T \) is the temperature [K].

The Arrhenius dependence for ZnO, ZT-a, and ZT-a sulfidation reactions was determined by measuring the initial sulfidation rate as a function of temperature. The experiments were performed in 2% H₂S–1% H₂–97% N₂. Figure 6 shows the resultant Arrhenius plots for ZnO, ZT-a, and ZT-a sulfidations. The intrinsic sulfidation rate for ZnO was greater than ZT-a and ZT-a at all temperatures between 400 and 800 °C, while the Arrhenius plots for ZT-a and ZT-a virtually overlapped. The kinetic constants obtained for ZnO and ZT-a sulfidation are listed in Table III. The activation energies for both ZnO and ZT-a sulfidation were approximately the same (10.3 kcal/mol and 9.3 kcal/mol, respectively). The major
difference was in the frequency factors. The frequency factor for ZnO sulfidation was approximately 3 times greater than that for Z2T-a. The lower frequency factor for the latter was probably caused by fewer reaction sites on the reactant surface due to the presence of titanium on the surface.

In contrast to the results obtained in this work, Woods et al. (1990) reported the sulfidation kinetics of Zn–Ti oxides to be independent of temperature in the range of 650–760 °C. This discrepancy is due to the fact that Woods et al. measured global sulfidation rates of Zn–Ti oxide pellets (3/16-in. diameter and \( L/D = 2.5 \)) under conditions not free from mass-transfer and pore diffusion limitations. Such measurements with pellets provide apparent reaction rates, are pellet-specific, and should not be used to obtain values for intrinsic kinetic parameters such as the activation energy.

The initial sulfidation rate reported in the present study for ZnO powders was approximately twice as fast as that reported by Westmoreland et al. (1977). This difference in sulfidation rate is believed to be due to differences in crystallinity. Better agreement of the sulfidation rate with Westmoreland et al. (1977) was obtained using a commercially purchased ZnO (EM Science, AR grade). Comparison of SEM micrographs of both ZnO types showed different crystal geometries present in each sample. The (EM Science) ZnO had a majority of rectangular crystals, while the ZnO prepared by the amorphous citrate technique consisted mainly of spherical crystals. It is known from the literature that exposure of different ZnO crystal faces can be obtained by varying the precursor (Krebs and Littbarski, 1981; Hindermann et al., 1988) during preparation. Variations in exposed crystal faces can cause differences in reactivity in structure-sensitive reaction systems.

Conversion Profiles of Bulk Zn–Ti–O Sorbents. The sulfidation reactions of three sorbents, ZnO, Z2T-a, and Z2T3-a, were studied in detail. Figure 7 shows the conversion profiles for these sorbents at 650 °C. Conversion was defined as follows:

\[
X = \frac{(W_i - W)}{(W_i - W_f)}
\]

where \( W \) is the weight, \( W_i \) is the initial weight, and \( W_f \) is the final weight at complete conversion assuming that the sorbent reacts completely to form ZnS and TiO\(_2\) (for the Zn–Ti–O sorbents).

For Z2T-a and Z2T3-a, the decrease of reaction rate at high conversion is attributed primarily to nonuniformity in the grain size distribution of the solids. SEM micrographs of Z2T-a and Z2T3-a showed the presence of both small spherical grains and larger plate-like grains. In the early portion of the conversion profiles for Z2T-a and Z2T3-a (Figure 7), the small grains were mainly reacting while at higher conversion all the small grains had reacted and reaction was due only to the larger plate-like grains. The effect of nonuniform grain size was verified by sulfidation of the solid Z2T-b, which was prepared by using a 2:1 mole ratio of citric acid to metal ions instead of the
different zinc titanate compounds are believed to react
initial sulfidation rate significantly different than sorbent
bent ZT which contained 20 wt%
Zn2Ti04
analyses of partially sulfided sorbents (Table IV), the
for the hetic experiments (1-3
used. This was a much larger
uniform reaction rate was measured for sorbent Z2T-b up
to very high conversions (Figure 9). The formation of a
product layer of ZnS and TiO2 around the unreacted solid
core also contributed to the slower reaction rate at higher
conversion. A more detailed discussion of the effect of
product layer diffusion on zinc titanate sulfidation is
presented in Lew et al. (1992b).
XRD analyses were performed on samples reacted in the
TGA at 650 °C in 2% H2S-1% H2-97% N2. To provide
sufficient amount of samples for analysis, 20-30 mg was
used. This was a much larger quantity than what was used
for the kinetic experiments (1-3 mg). On the basis of XRD
analyses of partially sulfided sorbents (Table IV), the
different zinc titanate compounds are believed to react
according to

\[
\begin{align*}
\text{ZnTiO}_3 + \text{H}_2\text{S} & \rightarrow \text{ZnS} + \text{TiO}_2 \\
\text{Zn}_2\text{TiO}_4 + \frac{3}{2}\text{H}_2\text{S} & \rightarrow \frac{3}{2}\text{ZnTi}_2\text{O}_6 + \frac{3}{2}\text{ZnS} + \frac{3}{2}\text{H}_2\text{O} \\
\text{Zn}_2\text{Ti}_2\text{O}_6 + 2\text{H}_2\text{S} & \rightarrow 2\text{ZnS} + 3\text{TiO}_2 + 2\text{H}_2\text{O}
\end{align*}
\]

No significant amount of free TiO2 was detected for the
Z2T-a sample sulfided to 48%. This indicates that Zn2-
TiO4 reacted much slower than Zn2TiO3. However, sorbent
ZT which contained 20 wt % Zn2TiO4, 35 wt %
Zn2Ti2O6, and 45 wt % ZnTiO3 (Table I) did not have an
initial sulfidation rate significantly different than sorbent
Z2T-b (100 wt % Zn2TiO4). The reason that no free TiO2
was detected in the partially reacted Z2T-a sorbent must
then be attributed to a rapid reaction of any TiO2 formed
with Zn2TiO4 to produce Zn2Ti3O6:

\[
\text{Zn}_2\text{TiO}_4 + 2\text{TiO}_2 \rightarrow \text{Zn}_2\text{Ti}_3\text{O}_6
\]

Physical Changes of Sorbents during Sulfidation.
Surface area changes along with morphological changes of
the Zn-Ti-O sorbents were examined. The samples were
sulfided in the TGA at 650 °C with 2% H2S-1% H2-97% N2.
To obtain sufficient quantity of samples for accurate
measurements of the surface area, a large amount (40-60
mg) of sample was used. The solids were sulfided to
approximately 90% conversion, and then their surface areas
were measured.

Typically, all Zn-Ti-O materials showed an increase in
surface area upon sulfidation. This in an agreement with
our previous reports with this type of sorbent (e.g., Fyty-
zani-Stephanopoulos et al., 1987). For Z2T3-a after 90%
sulfidation, the surface area increased from 2.3 to 2.8 m2/g.
By constrast, the surface area of sulfided ZnO was 1.7
m2/g, lower than the value for the fresh sorbent (2.4 m2/g).
On the basis of SEM micrographs of the sulfided samples,
it is apparent that while ZnS tends to sinter, TiO2
inhibits this sintering by acting as a physical barrier to
prevent growth of ZnS particles. Thus, TiO2 acts as a
dispersant of ZnS. SEM photographs of unreacted and
90-95% sulfided Z2T3-a are shown, respectively, in Figures
10 and 11. On the basis of EDS elemental analyses of the
surface, more sintered regions contained lower levels of
titanium. The sulfided region in Figure 11a contains
\(\text{Zn} / \text{Ti}\)atomic = 0.32 and \((\text{S} / \text{Zn})\)atomic = 1.0 and preserves
small grain sizes. In contrast, the more sintered region
shown in Figure 11b contains \(\text{Zn} / \text{Ti}\)atomic = 1.8 and
\((\text{S} / \text{Zn})\)atomic = 1.0.
To determine how different Zn-Ti-O compositions
affected the surface area of the sulfided solids, solids with
initially similar surface area were chosen for sulfidation.
All solids except for Z2T3-b were sintered (1000 °C, 1 h)
until they reached approximately the same surface area
(=0.8 m2/g). Z2T3-b was not subjected to any further heat
treatment beyond its initial calcination. The solids were
reacted at 650 °C in 2% H2S-1% H2-97% N2 for 90 min
or until ~90% sulfidation was reached. The surface areas
obtained for the sulfided solids are shown in Figure 12.
After sulfidation, the surface area of all solids increased.
The largest surface area increase after sulfidation was found with solids containing (Zn/Ti)$_{\text{atomic}}$ = 1. Increasing the amount of titanium in the solids beyond (Zn/Ti)$_{\text{atomic}}$ = 1 produced no further increase in the surface area. The formation of free TiO$_2$ with higher surface area cannot be invoked to explain the surface area increase of Zn-Ti-O solids upon sulfidation. In fact, when TiO$_2$ was calcined for the same length of time and at the same temperature as ZnO, the surface area of ZnO was 1.3 times higher than TiO$_2$. Therefore, low levels of TiO$_2$ are most effective in preserving ZnS dispersion and total surface area in the Zn-Ti-O sorbents.

**Effect of H$_2$**. Hydrogen reduces Zn-Ti-O and ZnO solids at the temperatures of interest in hot gas desulfurization ($\geq 600$ °C). In particular, ZnO is reduced approximately 3-10 times faster than Zn-Ti-O solids at temperatures in the range of 600-700 °C (Lew, 1990; Lew et al., 1992a). Small amounts of H$_2$O (~1% in the reactant gas stream) were shown (Lew, 1990; Lew et al., 1992a) to inhibit reduction of both Zn-Ti-O and ZnO solids, while further increasing the H$_2$O content to 8% did not have any additional effect on the reduction rate. From the reduction of partially sulfided Zn-Ti-O and ZnO solids, it appeared that H$_2$S had an inhibitory effect on reduction similar to H$_2$O. Comparative Arrhenius plots of the initial reduction and sulfidation rates are shown in Figure 13 for ZnO, Z2T-a, and Z2T3-a. The reduction rate is shown for a gas containing 10% H$_2$-3% H$_2$O-87% N$_2$, while sulfidation is for 2% H$_2$S-98% N$_2$. The point at which the initial reduction rate of ZnO became faster than its initial sulfidation rate was at 848 °C, while for Z2T3-a it was 942 °C. Consequently Zn-Ti-O solids can be used for the desulfurization of coal-derived fuel gas at higher temperatures than ZnO. The desulfurization temperature can be 94 °C higher with Z2T3-a than with ZnO. This higher operating temperature largely compensates for the lower rate of sulfidation of Z2T3-a relative to ZnO.

No change in the initial sulfidation rate was observed with the addition of various amounts of H$_2$ (0, 1, and 10%) in the gas stream at temperatures in the range of 400-800 °C. Typical sulfidation profiles for ZnO and Z2T-a at 800 °C with various hydrogen concentrations (1, 10, and 20%) are shown in Figure 14. For both ZnO and Z2T-a, it appears that little if any zinc loss took place based on the final weight of the solids. Both sorbents were completely sulfided (based on the initial sorbent weight). The absence of zinc loss is due to the particular configuration of our system (i.e., a hemispherical pan with a thin layer of reactant solid). Although little noticeable zinc loss took place, reduction did occur. Zinc vapor which formed as a result of reduction diffused toward the reactant gas subsequently reacting with H$_2$S to form a solid product of ZnS which was deposited on the pan. After sulfidation was completed, a white film was observed on the sample pan. Analysis of this film by atomic absorption spectroscopy identified the presence of zinc.

At high conversion, the reaction rate dropped faster when sulfidation was performed with a gas containing...
Figure 14. Effect of \( \text{H}_2 \) on the sulfidation conversion profiles at 800 °C for (a) ZnO and (b) Z2T-a.

Figure 15. SEM micrograph showing fine ZnS particles on the surface of ZnO after complete sulfidation at 800 °C in 2% \( \text{H}_2 \)-20% \( \text{H}_2\text{S} \)-bal. N\(_2\). only zinc loss but also weakening of the strength of the material by crack formations and the formation of fine particles.

In contrast to the dramatic gross structural changes observed with ZnO, minor structural changes were observed for Z2T-a sulfided at 800 °C in the presence of various hydrogen concentrations (1–20%). This is in agreement with the earlier finding that Zn-Ti-O sorbents were more resistant to reduction than ZnO (Lew, 1990; Lew et al., 1992a). No fine crystals or agglomerates were seen on the surface of the reacted solids.

Effect of \( \text{H}_2\text{O} \). Coal-derived gas streams contain steam in amounts depending on gasifier type and extent of quenching (10–50% \( \text{H}_2\text{O} \)). The effects of \( \text{H}_2\text{O} \) on the sulfidation kinetics of the sorbent were addressed in this work. Experiments were performed in a gas mixture consisting of 2% \( \text{H}_2\text{S} \)-1% \( \text{H}_2\text{O} \)-1% \( \text{H}_2 \)-96% N\(_2\) and 0.5% \( \text{H}_2\text{S} \)-1.9% \( \text{H}_2\text{O} \)-1% \( \text{H}_2 \)-96.6% N\(_2\). Water was introduced in saturated amounts at 25 °C in flowing \( \text{H}_2 \)-N\(_2\). In the absence of water vapor from the reactant gas stream, the calculated concentration of \( \text{H}_2\text{O} \) (produced during sulfidation) in the external film of the particle was approximately zero. Therefore, although the 1% \( \text{H}_2\text{O} \) used here was lower than what is typically found in coal-derived fuel gases (e.g., ~20% from a fluidized-bed KRW gasifier), it was much higher than what is found in the external film. Thus, any potential effect (e.g., poisoning) of water vapor on the sulfidation kinetics would be apparent in a gas containing 1% \( \text{H}_2\text{O} \). No such effect was found on the sulfidation rates of ZnO, Z2T-a, and Z2T3-a under the conditions used in this work.

Regeneration of Bulk Zn–Ti–O Sorbents. In order for Zn-Ti-O solids to be used commercially for the desulfurization of hot fuel gases, the sulfided solids must be regenerable. To determine the regenerability of Zn-Ti-O solids and their sulfidation performance after regeneration, two cycles of consecutive sulfidation–regeneration were performed with ZnO and Z2T-a. The results are shown in Figure 16 in terms of the dimensionless weight loss.

\[
\frac{W}{W_0} = \int_0^t \frac{dW}{W_0} dt
\]

where \( W \) is the instantaneous and \( W_0 \) the initial weight of the solid) versus the reaction time. Prior to the first cycle, the solids were reduced in 10% \( \text{H}_2 \)-90% N\(_2\) for 7 min. The partially reduced solids were then sulfided in 2% \( \text{H}_2\text{S} \)-98% N\(_2\). After sulfidation, regeneration was performed in air (21% O\(_2\)-79% N\(_2\)). High oxygen level was used in the regeneration to determine if any ZnSO\(_4\) was formed. Incomplete regeneration is due to the formation of ZnSO\(_4\). All reactions were performed at 650 °C.
As discussed previously, the more rapid decrease in sulfidation rate of sorbent Z2T-a, seen in Figure 16b, was due to the presence of nonuniform grain size distribution in the solid. In the first cycle, regeneration of Z2T-a and ZnO was essentially complete after 40–50 min. On the basis of the final weight after regeneration, little if any zinc sulfate (ZnSO₄) was formed during regeneration. In the second cycle, the sulfidation performance of ZnO became worse when compared with the first cycle. As shown in Figure 16a, the sulfidation rate in cycle 2 decreased noticeably after approximately 90% conversion (W/W₀ = 1.06). In contrast, the sulfidation of Z2T-a (Figure 16b) in cycle 2 was the same as in the first cycle. In the second regeneration, the performance of both Z2T-a and ZnO became slightly worse. After 40–50 min, regeneration of both Z2T-a and ZnO was about 95% complete.

Summary/Conclusions

The initial sulfidation rate of Zn–Ti–O sorbents measured with 90–125-μm particles in a TGA was 1.5–2 times slower than that of ZnO. At temperatures between 400 and 700 °C, similar activation energies (9–10 kcal/mol) were found for both Zn–Ti–O and ZnO sorbents, while lower frequency factors were measured for the Zn–Ti–O sorbents. Thus, it appears that the sulfidation of Zn–Ti–O proceeds by the same mechanism as ZnO sulfidation, but the presence of titanium serves to eliminate reaction sites. However, only a certain number of reaction sites are eliminated by titanium. Increasing the titanium content of the sorbents above 25 mol % (based on Zn–Ti stoichiometry) does not lead to a further decrease in the frequency factor.

No differences were measured in the sulfidation kinetics of different zinc titanate phases (i.e., Zn₂TiO₄, Zn₉Ti₃O₈, and ZnTiO₃).

The presence of titanium in ZnO inhibited sintering of ZnS. In fact, Zn–Ti–O sorbents showed an increase in their surface area after sulfidation.

No effect of hydrogen on the sulfidation kinetics of ZnO and Zn–Ti–O sorbents was observed for temperatures in the range of 400–800 °C. No zinc loss was evident (by weight change in the TGA) for either ZnO or sorbent Z2T-a. However, zinc vapor was produced at 800 °C as evidenced by cracks and fine particles observed on the surface of ZnO and deposits in the pan. These morphological features can be explained by ZnO reduction to zinc and water vapor followed by evolution of the product gases and subsequent reaction of Zn(g) with H₂S(g) to form fine particles of ZnS(s). Such structural effects were absent from the surface of Z2T-a particles after reaction at the same conditions as those for ZnO.

Zn–Ti–O sorbents allow raising the operating temperature for fuel gas desulfurization as a result of their lower ZnO reduction rate. For example, a solid with (Zn/Ti)atomic = 2/3 can operate at a temperature 94 °C higher than ZnO.

The choice of sorbent composition for desulfurization should be based on the amount of reduction tolerated and the sulfur loading desired. A higher percentage of titanium is needed in order to decrease the reduction rate (Lew et al., 1992a). This will be at the expense of sulfur loading. For example, a solid with (Zn/Ti)atomic = 2/3 which has a 9 times lower reduction rate than ZnO, has a sulfur loading of only 0.16 g of sulfur/g of sorbent (based on complete conversion to ZnS). In contrast, ZnO has a sulfur loading of 0.39 g of sulfur/g of sorbent.

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Registry No. ZnO, 1314-13-2; zinc titanate, 12651-25-1.

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Mechanisms for Lowering of Interfacial Tension in Alkali/Acidic Oil Systems: Effect of Added Surfactant

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Experimental studies are conducted in order to determine the physicochemical mechanisms responsible for lowering of interfacial tension in alkali, surfactant, and surfactant-enhanced alkali/acidic oil systems. A well-defined model oil is chosen to examine the influence of various surfactants and surfactant mixtures, such as oleic acid and its ionic counterpart, sodium dodecyl sulfate, petroleum sulfonate, and isobutanol, on equilibrium interfacial tension. With added surfactant alone, the interfacial tension goes through an ultralow minimum with increasing acid concentration. This proves for the first time that the un-ionized acid species plays a major role in affecting interfacial tension, and appears to be the key element in the synergistic process taking place between the added surfactant and the ionized acid species. The un-ionized acid species partitions the added surfactant out of the aqueous phase, and the minimum in interfacial tension occurs when the partition coefficient is about unity. When alkali is added, the low interfacial tension is not lost, but actually shifts to different acid concentrations in a systematic way.

Introduction

It is well-known that interfacial tension between a surfactant solution and a hydrocarbon can become ultralow. A number of variables, such as salinity (Chan and Shah, 1980), oil chain length (Chan and Shah, 1980), alcohol concentration and type (Miller and Neogi, 1985), surfactant concentration (Chan and Shah, 1980) and type (Doe et al., 1977, 1978a,b), and temperature (Miller and Neogi, 1985), have been found to affect the position of the interfacial tension minimum. Chan and Shah (1981) observed two regions of ultralow interfacial tension as surfactant concentration is increased. One region is at low surfactant concentrations of about 0.1 wt % (a two-phase region), and the other is at high surfactant concentrations of about 4 wt % (a three-phase region). In the two-phase region, the ultralow interfacial tensions are due to the presence of a saturated monolayer at the interface (Chan and Shah, 1980; Pouchelon et al., 1981). In the three-phase region, the ultralow interfacial tensions are due to a critical behavior (Fleming and Vinatieri, 1979, 1981; Fleming et al., 1980). Chan and Shah (1980) also found that an increase in salinity causes partitioning of the surfactant from the aqueous to the oil phase, and interfacial tension is ultralow when the partition coefficient is about unity. Chan and Shah (1981) also showed that the interfacial tension goes through an ultralow minimum when the oil chain length is increased, and the minimum again occurs when the partition coefficient is about unity.

With the addition of a small amount of surfactant to the alkaline solution, the interfacial tension can become lower than either surfactant or alkali alone (Schuler et al., 1986). The reason for this synergy is not well-known. In this paper, we investigate the interaction of the un-ionized acid

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