**MECHANISTIC AND KINETIC STUDIES OF HIGH-TEMPERATURE COAL GAS
DESULFURIZATION SORBENTS**

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SUMMARY

This final report describes the work performed under the sponsorship of the U.S. DOE-University Coal Research Program, Grant No. DE-FG22-88PC88927 on "Mechanistic and Kinetic Studies of High-Temperature Coal Gas Desulfurization Sorbents." The work was conducted in the Department of Chemical Engineering at the Massachusetts Institute of Technology. The grant supported the doctoral work of Susan Lew, a graduate student of Chemical Engineering at M.I.T., who completed her Ph.D. thesis in late 1990.

The overall objective of this project was to investigate the properties of and evaluate bulk mixed oxides of zinc and titanium for hot fuel gas desulfurization. ZnO neat was also investigated as a base case. The selection of Zn-Ti-O for study in this project was based on earlier work at M.I.T. that had identified Zn-Ti-O solids as more resistive to reduction than zinc oxide or zinc ferrite materials undergoing sulfidation at temperatures exceeding 600°C.

A basic research approach was undertaken in this project aimed at improving our understanding of the properties and performance of the mixed oxides of zinc and titanium and determining the potential benefits of Zn-Ti-O for regenerative hot gas cleanup applications. Thus, comparative studies of the kinetics of reduction and sulfidation of zinc titanate and zinc oxide were carried out. Parametric effects of H_2 and H_2O vapor were investigated. Also, the structural effects of reductive sulfidation were examined on both types of sorbents. To aid the analysis, the sorbents were prepared from organic precursors in macroporous granular form, thus, eliminating pore diffusion resistances. Experiments were conducted in a thermogravimetric apparatus (TGA) operated under conditions free of gas-film diffusion limitations. Hence, the measured reaction rates were controlled only by intrinsic sorbent kinetics and/or product layer diffusion.

The reduction of bulk ZnO and mixed oxides of zinc and titanium of various Zn:Ti atomic ratios and Zn-Ti-O crystalline phases was studied in the TGA in H_2 - H_2O - N_2 gas mixtures at 550-1050°C. Zinc titanates were reduced more slowly to volatile elemental zinc than single zinc oxide. In the absence of water vapor, activation energies of 24 and 37 kcal/mol were measured for ZnO and Zn-Ti-O, respectively. Solids with Zn-Ti atomic ratio of 3:1 had significantly lower reduction rates than ZnO. Higher relative concentrations of titanium did not significantly change the reduction rate. Different zinc titanate phases, i.e., Zn_2TiO_4 , $ZnTiO_3$ and $Zn_2Ti_3O_8$, had similar reduction kinetics. The addition of water vapor inhibited reduction and resulted in a change in activation energy to 44 kcal/mol for both ZnO and Zn-Ti-O solids. Similar to H_2O , H_2S inhibited the initial reduction rate of ZnO and Zn-Ti-O materials.

Based on the kinetic experiments, a two-site reduction model was proposed for ZnO reduction. One type of sites is characterized by a rapid reduction rate but is poisoned by water vapor as well as by the presence of titanium atoms in the solid. The other type of sites has a lower reduction rate, is not poisoned by H_2O , and is slowly eliminated by the presence of titanium. The geometric interaction of titanium with the two types of reduction sites of zinc oxide is believed to cause elimination of these sites. Whether this property is unique to titanium is not clear at the present time. In contrast to this, it is known from the

literature that addition of iron oxide into ZnO in the form of the compound zinc ferrite, ZnFe_2O_4 , provides no stability to ZnO against reduction. This may be due to the fact that ZnFe_2O_4 breaks up into ZnO and Fe_3O_4 (or lower valence iron oxides) in a reducing gas atmosphere. In the present study no free ZnO was found in the zinc titanate compounds reacted in hydrogen. Perhaps the ability of titanium to remain intimately associated with ZnO and, thus, possibly the reactive sites, in a reducing gas atmosphere can explain why Zn-Ti-O solids have lower reduction rates than Zn-Fe-O solids.

The sulfidation of bulk ZnO and mixed oxides of zinc and titanium of various compositions and Zn-Ti-O crystalline phases in H_2S - H_2 - H_2O - N_2 gas mixtures was investigated in the TGA over the temperature range of 400-800°C. The incorporation of TiO_2 into ZnO stabilizes the latter against reduction to volatile elemental zinc and, thus, allows raising the operating temperature for desulfurization, i.e. the cross-over temperature of the initial reduction and sulfidation rates, e.g. by as much as 94 degrees Celsius for solids with $(\text{Zn}/\text{Ti})_{\text{atomic}} = 2/3$. The initial sulfidation rate of Zn-Ti-O with $(\text{Zn}/\text{Ti})_{\text{atomic}} \leq 3$ was approximately 1.5-2 times slower than for ZnO. Different zinc titanate phases (i.e. Zn_2TiO_4 , ZnTiO_3 and $\text{Zn}_2\text{Ti}_3\text{O}_8$) 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 H_2 or H_2O was observed on the initial sulfidation rate. However, the presence of H_2O enhanced the sintering of both ZnO and Zn-Ti-O sorbents undergoing sulfidation.

Important structural differences between zinc titanate and zinc oxide sorbents were discovered in this work: (i) the presence of titanium in ZnO inhibits the sintering of ZnS. In fact, Zn-Ti-O sorbents show a measurable surface area increase after sulfidation. (ii) The morphology (and finally integrity) of ZnO is severely hampered in high hydrogen (> 10 mol%)-containing sulfidation gases. At 800°C, fine particles and cracks were observed in sulfided ZnO as a result of ZnO reduction and subsequent vapor phase reaction between Zn and H_2S to form ZnS. These structural effects were largely absent in Zn-Ti-O solids, and their absence provides the major motivation for the use of zinc titanates.

On the basis of microscopic solid surface analyses, the random grain model, which allows for randomly overlapping grains, was used to describe the sulfidation of zinc oxide and zinc-titanium oxide powders. This model more realistically simulated the grain structure of both the ZnO and Zn-Ti-O sorbents. A unimodal and a bimodal grain size distribution, respectively, for ZnO and Zn-Ti-O, with the random grain model successfully predicted the sulfidation profiles of each sorbent type.

Resistances to reaction were attributed to intrinsic sulfidation kinetics (surface reaction) and diffusion through the product layer. The product layer diffusion coefficient, D_e , was used as a fitting parameter in the model. As the relative amount of the titanium in the sorbent was increased, the product layer diffusion coefficient decreased. Similar activation energies (26.6 kcal/mol) were obtained for the product layer diffusion coefficient of ZnO and Zn-Ti-O solids undergoing sulfidation. From the similarity in activation energies, and the very low diffusivity through TiO_2 -coated ZnO crystals, it is proposed that for both types of sorbents diffusion occurs primarily through ZnS. TiO_2 merely decreases the cross-sectional area for diffusion and increases the tortuosity. Although a drawback of

Zn-Ti-O sorbents over ZnO is their lower D_e , at high temperatures and with high sorbent surface area, product layer diffusion is relatively fast compared to intrinsic sulfidation kinetics.

Structural advantages may offset the kinetic and low-capacity drawbacks of TiO_2 -containing ZnO. However, all these factors should be weighed in determining the most suitable Zn-Ti-O composition for hot coal gas desulfurization. Additional fundamental work on the structural stability of this type of sorbents and ways to promote it are needed to guide further development of the materials. Also, studies of the regeneration chemistry and kinetics and of the performance regenerability of zinc titanates are needed to justify selection of these sorbents over other competing systems as fully regenerable, attrition-resistant, high-temperature sulfur sorbents, suitable for commercial applications.

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1. INTRODUCTION

Coal gasification integrated with combined-cycle power generation (IGCC) and coal gasification followed by oxidation in a molten carbonate fuel cell are emerging as viable methods for more efficient and cleaner power generation. Cost analyses of integrated gasifier utilizing conventional gas cleanup (i.e. liquid scrubbing) show that the capital cost for construction of an oxygen-based Texaco IGCC plant and the associated operating cost for electricity generation are competitive with conventional coal-fired steam plants (Gluckman and Louks, 1982). Increasingly more stringent emission control requirements are expected to increase the cost advantage of both IGCC and coal gasification-molten carbonate fuel cells. With the emergence of these technologies as promising routes for power generation, an emphasis has been placed on improving the efficiencies and decreasing the costs of these processes. One focus has been fuel gas cleanup. This is important both for environmental reasons as well as equipment protection (e.g. from fouling). The other focus has been on increasing the value of the fuel gas temperature that the gas turbine and fuel cell can accept. Higher temperature increases the efficiency of the process.

The fuel gas produced from coal gasification can be used either in a combined cycle power plant or a fuel cell. The fuel cell offers the advantage of higher efficiencies over the combined cycle plant. The combined cycle consists of a gas turbine in series with a steam turbine. The maximum efficiency for this type of process is limited by the Carnot cycle limitation. The fuel cell, on the other hand, can directly convert chemical energy to electrical energy. Thus, higher efficiencies are possible. However, this technology is at a more early stage of development than the combined-cycle process.

Research in this project has focused on high-temperature regenerative sulfur removal from coal-derived fuel gas streams. In the gasifier, the sulfur in the coal is released primarily as hydrogen sulfide. The required efficiency of H_2S removal for the coal-derived fuel gas depends on the method of power generation. For a combined-cycle power plant, the H_2S level in the coal gas must be ≤ 100 ppmv in order to meet current environmental regulations. The fuel gas must be purified to less than 1 ppmv for H_2S for use in a molten carbonate fuel cell to prevent poisoning of the nickel-based electrode.

Several commercial methods exist for the removal of hydrogen sulfide. These processes are based on the reversible physical absorption of H_2S by a solvent such as methanol (Rectisol process) or dimethyl ether of polyethylene glycol (Selexol process). However, a major disadvantage of these commercial methods for the purification of fuel gas used in power generation facilities is that the hot fuel gas must be cooled down to near ambient temperatures and then reheated prior to its final combustion.

Direct removal of H_2S from the hot fuel gas can significantly improve the process thermal efficiency (Marqueen et al., 1986). A high inlet gas temperature to the gas turbine and fuel cell is essential for high efficiency. Hot gas cleanup will eliminate the costs of heat exchangers to cool down the fuel gas, reheating equipment, and expensive waste water cleanup process. Figure 1.1 shows a diagram of a proposed integrated combined-cycle power plant in which hot gas cleanup is incorporated.

Metal oxides have been considered for H_2S removal by a sulfidation-regeneration scheme with the following overall reactions:

Figure 1.1 A proposed integrated combined-cycle power plant utilizing hot gas cleanup (Marqueen et al., 1986).

In addition, there is the possibility of solid reduction by H_2 and CO:

Reactions 1.1 and 1.2 can ideally be repeated many times. The sulfur product, sulfur dioxide (SO_2), produced during regeneration is in a much more concentrated stream than hydrogen sulfide is in the untreated fuel gas. It can be sent to a sulfur recovery unit to produce elemental sulfur. Various metal oxide sorbents, such as iron, zinc, calcium, and copper oxides, have been considered to remove H_2S at high temperatures (MERC, 1978). However, each of these oxides has its own distinct set of advantages and disadvantages. Calcium oxide is inexpensive and can meet the environmental regulations regarding H_2S level (≤ 100 ppmv). However, it cannot remove H_2S to the level required by a fuel cell. Calcium sulfide is non-regenerable. This leads to the additional cost of solid waste removal. Iron oxide has fast sulfidation kinetics and is regenerable. However, iron oxide, Fe_2O_3 , is reduced to Fe_3O_4 by the H_2 and CO present in coal gases. Fe_3O_4 has low thermodynamic efficiency (equilibrium H_2S level > 100 ppmv). Further reduction to FeO and formation of iron carbides are additional problems of iron oxide sorbents. Copper oxide is similarly reduced to Cu metal which is an inferior H_2S sorbent (although still better than Fe_3O_4). Use of a dispersant phase, e.g. aluminum oxide, is required to prevent sintering of the copper metal and loss of sorbent capacity. ZnO has better sulfidation equilibria than copper metal and can be used in unsupported form as a regenerable H_2S sorbent. Subequilibrium H_2S levels (< 1 ppmv) can be attained under certain conditions with ZnO due to additional chemisorption of H_2S (Flytzani-Stephanopoulos et al., 1985). However, at temperatures

above 600°C, volatile elemental zinc is formed by the reaction:

The resulting sorbent loss and adverse structural changes with repeating cycling (sulfidation-regeneration) represent major problems with zinc oxide sorbents.

Mixed metal oxides have potential advantages over single component oxides for the regenerative removal of hydrogen sulfide from coal-derived gases at high temperatures. Mixed oxides containing Cu-Al, Cu-Fe-Al, Zn-Fe, and Zn-Ti have been studied in this laboratory (Flytzani-Stephanopoulos et al., 1987; Lew et al., 1989) as well as by others (Tamhankar et al., 1986; Focht et al., 1988; Patrick et al., 1989; Sa et al., 1989; Ayala et al., 1989). The most extensively studied mixed oxide to date is zinc ferrite (ZnFe_2O_4), which showed somewhat better capacity and regenerability than ZnO in initial work carried out at DOE/METC (Grindley and Steinfeld, 1981). However, the reduction rate of ZnO to volatile zinc is not affected by the presence of iron oxide. Mixed oxides of zinc and titanium were selected for detailed investigation in this project. Earlier studies in this laboratory using a packed-bed reactor in sulfidation-regeneration cycles (Flytzani-Stephanopoulos, 1987; Lew, 1987; Lew et al., 1989), had identified Zn-Ti-O sorbents as more resistive to reduction than zinc oxide neat. In addition, the sulfidation performance of the mixed oxides was not adversely affected.

1.1 PROJECT OBJECTIVES

The overall objective of this project was to investigate the properties of and evaluate mixed oxides of zinc and titanium for hot fuel gas desulfurization. Uncombined ZnO was also investigated as a base case. Detailed investigation of the reduction and sulfidation

reactions of Zn-Ti-O sorbents was performed. The intrinsic kinetics and the product layer diffusion rates in reduction and sulfidation were determined. Kinetic experiments with sorbents containing various Zn/Ti atomic ratios were performed. Chemical phase and structural transformations were followed by various methods. The results were compared to similar experiments performed with ZnO. The purpose of these experiments was to determine how the presence of titanium dioxide affects the reduction and sulfidation of ZnO. This information would be used to identify and select the sorbent composition that gives the best combination of low reduction rate and acceptable sulfidation performance at temperatures exceeding 600°C.

1.2 DESCRIPTION OF PROJECT TASKS

The major tasks of this project were to (i) synthesize and characterize Zn-Ti-O materials; (ii) measure the reduction kinetics of Zn-Ti-O and ZnO; (iii) measure the sulfidation kinetics and identify structural changes of the sorbents in reductive sulfidation; (iv) develop models of the sulfidation of ZnO and Zn-Ti-O sorbents; and (v) evaluate the potential of Zn-Ti-O sorbents for hot coal gas desulfurization. Sections 2-6 of this report describe the work performed in each of the project tasks in the order given above.

In Section 2, the preparation of various bulk Zn-Ti-O solids using a complexation method with citric acid is discussed. Various zinc titanate phases, formed as a function of temperature and Zn/Ti ratio, were determined by X-ray diffraction. Physical properties (i.e. surface areas and pore volumes) of Zn-Ti-O solids were compared to ZnO. High surface area is desirable because it enhances reaction rates. High pore volume ensures that pore diffusion is not limiting and prevents pore plugging from occurring.

In Section 3, the reduction characteristics of various Zn-Ti-O solids are compared to ZnO. The intrinsic reduction kinetics of Zn-Ti-O solids as a function of Zn/Ti ratio and crystalline phases were investigated to determine the mechanism of reduction and how titanium dioxide interacts to inhibit reduction. The effect of H₂O was examined because not only is it a major component (10-50%) in coal gases, but also because of its inhibitory effects on ZnO reduction (Hegedus and Kiss, 1966; Flytzani-Stephanopoulos et al., 1987). Comparisons of the reactivity of bulk Zn-Ti-O sorbents with a ZnO single crystal coated with a thin film of TiO₂ were performed. The purpose of these experiments was to determine whether similar inhibition in reduction could be obtained by this method of preparation. The reduction experiments were compared with similar sulfidation experiments of the TiO₂-coated single crystal of ZnO to determine if any inhibition in reduction rate was at the cost of similar inhibition in sulfidation.

Sulfidation of various Zn-Ti-O and ZnO solids is described in Section 4. The effects of Zn/Ti ratios and zinc titanate phases on sulfidation were determined. Parameter studies were performed examining the effects of temperature and hydrogen sulfide, hydrogen and water vapor concentrations. Structural changes (i.e. surface morphology and surface area) and chemical phase changes were followed with the extent of sulfidation.

In Section 5, modeling of the sulfidation conversion profiles of ZnO and Zn-Ti oxides is presented. Different gas-solid models (e.g. the grain model) were investigated to calculate the product layer diffusion coefficients. The effects of titanium dioxide on the product layer diffusion coefficient are discussed. Finally, Section 6 summarizes the major conclusions of this project with recommendations for future work.

2. PREPARATION OF ZN-TI-O MATERIALS

2.1 BACKGROUND

Phase formation in the Zn-Ti-O system has been of considerable interest because of the importance of zinc titanates as white pigments and as fusion cast thermistors. In most of the early literature (Cole and Nelson, 1938; Dulin and Rase, 1960; Bartram and Slepety, 1961; Sheinkman et al., 1977), specific zinc titanate phases were prepared by mixing slurries of ZnO and TiO₂, drying the mixture, and calcining the mixture for an extended period of time. For example, Cole and Nelson (1938) required calcination at 1000°C for 20 h to completely react $2\text{ZnO} + \text{TiO}_2$. The extended calcination period was required in order to obtain sufficient compositional homogeneity. Because the diffusional paths between reactants are quite large (*ca.* 10^6 Å), long calcination times are required to ensure complete mixing of the reactants on the atomic scale. The final product from this preparation is often of low surface area, highly crystalline, and may possess poor homogeneity.

In more recent studies (Reddy et al., 1984; Lercher et al., 1984; Yamaguchi et al., 1987), zinc titanates have been prepared by a hydrolysis-pyrolysis technique. Because of the smaller reactant diffusion length, better compositional homogeneity can be achieved with this method. Thus, lower calcination temperatures and shorter calcination times are possible. However, in this method, the composition is restricted by the stoichiometric requirement of the precipitate. Also, due to the change in the composition of the liquid medium as the precipitate is formed, there may be some problems with maintaining the homogeneity of the product.

Synthesis of mixed oxides by complexation with citric acid can yield homogeneous and

highly dispersed mixed oxides. This technique (Marcilly et al., 1970; Courty et al., 1973), produces an amorphous, completely homogeneous solid obtained by evaporating a solution of metallic ions and a complexing polyfunctional hydroxyacid. Because of the intimate mixing of the metal ions, lower calcination temperatures than for the hydrolysis-pyrolysis technique can be used to achieve desired chemical phases. Since any initial stoichiometry of metal ions can be used, this method can potentially produce new multi-component mixed oxides. Villa et al. (1987) prepared zinc titanates by the complexation technique as catalysts for the synthesis of alcohols from carbon monoxide and hydrogen. They found that zinc titanates prepared by this method were more homogeneous with a moderately high surface area than zinc titanates prepared by a hydrolysis-pyrolysis technique.

In this project, Zn-Ti mixed oxides were prepared by complexation with citric acid. Various Zn-Ti-O compositions and calcination temperatures were used to determine their effects on the formation of various chemical phases and physical properties. These results were compared with those found in the literature.

2.2 EXPERIMENTAL

2.2.1 Zn-Ti-O Preparation

The mixed metal oxides were prepared by the complexation method with citric acid. Preparation was performed by dissolving citric acid monohydrate and $\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ (zinc acetate dihydrate) in water. One mole of citric acid was used for each gram-equivalent of metal ions (Zn+Ti). Acetic acid was added to $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$ (titanium (IV) isopropoxide, TTIP) in a 3:1 volumetric ratio to prevent the precipitation of titanium when it is added to the aqueous solution. The TTIP-acetic acid solution was slowly added to the

aqueous solution. The product of partial hydrolysis of TTIP formed was dissolved by stirring the solution. The relative amounts of TTIP and zinc precursor were varied according to the desired Zn/Ti ratio of the product.

Evaporation of the liquid was performed in a rotary evaporator at 65-75°C under vacuum (26-29 in. Hg). It was stopped when the viscosity increased to the point where discharge of the liquid became difficult. Evaporation was completed in a vacuum oven (29 in. Hg) for 4-6 h at 70-80°C. A white amorphous foam was formed. The foam was calcined in a furnace at the desired temperature under a stream of air to produce the final mixed oxide product.

2.2.2 Chemical and Physical Sorbent Analyses

To quantitatively determine the amount of zinc and titanium in the solid, atomic absorption analyses were performed with a Perkin Elmer 360 Atomic Absorption (AA) Spectrophotometer. The Zn-Ti-O solids were dissolved in a hot solution of HF:HCl:H₂O. To completely dissolve the solid, it was necessary to heat the solution containing the solid to 80-90°C for several hours. The relative concentrations of zinc and titanium ions in the solution were measured by AA. Zinc concentrations were determined at a wavelength of 213.9 nm using an air-acetylene flame for ionization. Titanium concentrations were determined at 365 nm with a nitrous oxide-acetylene flame.

The crystalline phase compositions were determined with a Rigaku RU300 X-ray diffractometer using Cu (K α) radiation. The X-ray tube was operated at 200 mA and 50 kV. A diverging slit of 1°, scattering slit of 1°, and receiving slit 0.3° were used. Solid samples were finely crushed (<325 mesh) and slurried in a polymer solution. Grinding the

solids to a fine size reduces preferred orientation and microabsorption effects. Preferred orientation is a major source of intensity error. Microabsorption is the effect of the solid particles geometry on the X-ray intensities diffracted by the solid. Microabsorption is affected by the surface roughness and bulk porosity of the solid. The slurry was spread on a glass slide and heated in an oven to evaporate the liquid. X-ray diffraction patterns in the range 10° to 100° were obtained. For powders containing multi-components, it is possible to estimate the relative concentration of each component by measuring the intensity of the diffraction pattern (Klug and Alexander, 1954).

The surface areas of the solids were determined with a Micromeritics Flow Sorb II 2300 BET apparatus. The solids were degassed at 220°C to remove any adsorbed H_2O . The surface areas were determined by the BET method using a 30% N_2 -70% He gas. A single point method technique was used to determine the surface area. The pore volume and corresponding pore size distribution of the solids were measured by mercury porosimetry using a Micromeritics Autopore 9200. Pressure as high as 60,000 psia can be applied. This is equivalent to a pore radius of $0.0015\ \mu\text{m}$. All the measurements were performed from 5 to 60,000 psia (18 - $0.0015\ \mu\text{m}$).

The surface morphologies of the solids were observed using a Cambridge Scientific Instruments Stereoscan 250. The solid sample was adhered to a standard SEM specimen mount coated with graphite paint. The sample was then coated with a thin layer of gold by vapor phase deposition to provide the necessary electric conductivity and to prevent charge buildup on the sample. (For samples which contained sulfur, coating must be performed with palladium because of the overlap of the gold and sulfur X-ray fluorescence peaks).

The SEM has an additional Tracor Northern TN-5400 X-ray analyzer for quantitative energy dispersive X-ray spectrometry (EDS).

2.3 PRESENTATION AND DISCUSSION OF SOLIDS PREPARATION

2.3.1 Chemical Phase Formation

Zinc titanate phase formation was investigated as a function of Zn/Ti ratio and calcination temperature. Solids with Zn/Ti atomic ratios ranging from 2/3 to 1/0 were calcined at temperatures from 500 to 1000°C. In Table 2.1, the crystalline phases formed as a function of temperature (500-800°C) are listed for Z2T3 (2 Zn:3 Ti), ZT (1 Zn:1 Ti), and Z2T (2 Zn:1 Ti). Figures 2.1 and 2.2 show examples of the typical XRD diffraction patterns obtained for Z2T and Z2T3 calcined at 500-800°C for 4 h. The increasing intensity as the diffraction angle decreased was due to the contribution of air scattering to the background intensity. At very low 2θ angles, the background intensity increased due to the grazing incident beam. The phase transformations observed with increasing temperature are:

Z2T3

500°C: amorphous ($\text{Zn}_2\text{Ti}_3\text{O}_8$ and/or $\alpha\text{-Zn}_2\text{TiO}_4$) → 600°C: ZnTiO_3 , TiO_2 (rutile), small amounts of $\text{Zn}_2\text{Ti}_3\text{O}_8$ and/or $\alpha\text{-Zn}_2\text{TiO}_4$ → 700°C: ZnTiO_3 , TiO_2 (rutile), $\alpha\text{-Zn}_2\text{TiO}_4$, $\text{Zn}_2\text{Ti}_3\text{O}_8$, small amounts of ZnO → 800°C: ZnTiO_3 , TiO_2 (rutile), $\alpha\text{-Zn}_2\text{TiO}_4$, ZnO

ZT

500°C: amorphous ($\text{Zn}_2\text{Ti}_3\text{O}_8$ and/or $\alpha\text{-Zn}_2\text{TiO}_4$) → 600°C: ZnTiO_3 , $\text{Zn}_2\text{Ti}_3\text{O}_8$ and $\alpha\text{-Zn}_2\text{TiO}_4$ → 700°C: $\alpha\text{-Zn}_2\text{TiO}_4$, ZnTiO_3 , ZnO, TiO_2 (rutile) → 800°C: $\alpha\text{-Zn}_2\text{TiO}_4$,

Table 2.1 Crystalline Phases Formed at Various Temperatures.

Sample ¹	Temperature (°C)	Crystalline Phase (wt %)				
		ZnO	α -Zn ₂ TiO ₄	Zn ₂ Ti ₃ O ₈	ZnTiO ₃	TiO ₂ (rutile)
Z2T	500 ²	30	70-x	x	0	0
	600	25	75-x	x	0	0
	700	20	57	0	23	0
	800	10	70	0	20	0
ZT	500 ³	0	0	0	0	0
	600	0	54-x	x	46	0
	700	20	23	0	40	17
	800	23	43	0	0	34
Z2T3	500 ²	0	0	0	0	0
	600	0	0	0	67	17
	700	0	7	8	64	21
	800	9	16	0	43	32

¹ Prepared by the amorphous citrate technique with Ti (IV) isopropoxide and zinc acetate as precursors. Calcined for 4 h.

² Very broad peaks.

³ Amorphous, Zn₂TiO₄ or Zn₂Ti₃O₈ might be present.

Figure 2.1 XRD patterns of Z2T3 (2 Zn : 3 Ti) calcined at 500-800 C for 4 h.

Figure 2.2 XRD patterns of Z₂T (2 Zn : 1 Ti) calcined at 500-800 °C for 4 h.

ZnO, TiO₂(rutile)

Z2T

500°C: Zn₂Ti₃O₈ and/or α-Zn₂TiO₄, ZnO → 600°C: Zn₂Ti₃O₈, α-Zn₂TiO₄, ZnO

→ 700°C: α-Zn₂TiO₄, ZnTiO₃, ZnO → 800°C: α-Zn₂TiO₄, ZnTiO₃, ZnO

At 500 and 600°C, the peaks of all solids are very broad which indicates the presence of amorphous material. In contrast, a fully crystalline material would be characterized by peaks whose shape approaches that of a delta function. At these temperatures, it was difficult to distinguish between α-Zn₂TiO₄ and Zn₂Ti₃O₈ because of the broadness of the peaks. The diffraction lines of these two phases are quite close, and the experimentally measured patterns were not well-resolved. The formation of ZnO at temperatures between 700-800°C is probably due to reduction by residual carbon followed by oxidation to form ZnO. This is discussed further in Section 2.3.2. A phase diagram showing the chemical phase formation as a function of Zn/Ti is shown in Figure 2.3. The solids were calcined at 720°C for 12 h with Zn/Ti ratio ranging from 2/3 to 1/0. These solids are completely crystalline. Figure 2.4 shows the XRD pattern of Z2T calcined at 720°C for 12 h. The higher crystallinity in this case made it easier to resolve the peaks of Zn₂Ti₃O₈ and α-Zn₂TiO₄. With increasing relative concentration of titanium, the phase transformation follows ZnO → Zn₂TiO₄ → ZnTiO₃, Zn₂Ti₃O₈ → TiO₂. All solids with Zn/Ti ≥ 2, form Zn₂TiO₄ and/or ZnO. With higher concentration of titanium, all three zinc titanate phases (Zn₂TiO₄, ZnTiO₃ and Zn₂Ti₃O₈) are stable. At 1000°C, Zn₂TiO₄ is stable. Solids containing either ZnTiO₃ or Zn₂Ti₃O₈ form Zn₂TiO₄ and TiO₂ at 1000°C.

There are some differences between the results of this work and the work of others.

Figure 2.3 Chemical phase formation as a function of Zn-Ti composition of solids calcined at 720°C for 12 h.

Figure 2.4 XRD patterns of Z2T (2 Zn : 1 Ti) calcined at 720 C for 12 h.

All previous investigators (Cole and Nelson, 1938; Dulin and Rase, 1960; Bartram and Slepety's, 1961; Reddy et al., 1984; Yamaguchi et al., 1987) agree that the phase Zn_2TiO_4 is formed when either $\text{Zn}/\text{Ti} \geq 2$ or the calcination temperature is $\geq 1000^\circ\text{C}$. Dulin and Rase (1960) found that ZnTiO_3 is stable up to $925 \pm 25^\circ\text{C}$ while Yamaguchi et al. (1987) found a slightly higher temperature (965°C). Above these temperatures, ZnTiO_3 decomposes into Zn_2TiO_4 and rutile TiO_2 . However, for lower Zn/Ti ratios and low calcination temperatures, substantial disagreement in the zinc titanate phase formation exists. Table 2.2 summarizes these findings. The major difference is that some investigators reported the formation of ZnTiO_3 and Zn_2TiO_4 or $\text{Zn}_2\text{Ti}_3\text{O}_8$ and Zn_2TiO_4 . Cole and Nelson (1938) observed the formation of Zn_2TiO_4 - TiO_2 solid solutions. However, these solid solutions are believed to be the results of poorly resolved Zn_2TiO_4 or $\text{Zn}_2\text{Ti}_3\text{O}_8$ reflections (Bartram and Slepety's, 1961). Bartram and Slepety's (1961) and Sheinkman et al. (1977) found that the type of zinc titanate phase formed depends on the titanium dioxide starting material. Combination of ZnO with anatase forms $\text{Zn}_2\text{Ti}_3\text{O}_8$ as well as Zn_2TiO_4 , while with rutile, ZnTiO_3 and Zn_2TiO_4 are formed. From their results, Sheinkman et al. (1977) proposed the following reactions:

In contrast, Dulin and Rase (1961) found that ZnTiO_3 and Zn_2TiO_4 are formed from the anatase phase of TiO_2 . Yamaguchi et al. (1987) proposed an alternate reaction scheme. Upon heating (at a rate of $10^\circ\text{C}/\text{min}$) the hydrolysis products of $\text{Ti}(\text{OC}_3\text{H}_7)_4$ and

Table 2.2 Stable zinc titanate phases for Zn/Ti < 2 and temperatures below 1000°C.

<u>Literature Source</u>	<u>Preparation Method</u>	<u>Zinc Titanate Phase</u>
Cole and Nelson (1938)	ZnO-TiO ₂ solid reaction (600-1000°C)	Zn ₂ TiO ₄ -TiO ₂ solid solutions
Dulin and Rase (1961)	ZnO-TiO ₂ (anatase) solid reaction (750-925°C)	Zn ₂ TiO ₄ and ZnTiO ₃
Bartram and Slepety's (1961)	ZnO-TiO ₂ (hydrous anatase) solid reaction	Zn ₂ TiO ₄ and Zn ₂ Ti ₃ O ₈
	ZnO-TiO ₂ (hydrous rutile) solid reaction (600-900°C)	ZnTiO ₃
Sheinkman et al. (1977)	ZnO-TiO ₂ (anatase) solid reaction (800°C)	Zn ₂ TiO ₄ and Zn ₂ Ti ₃ O ₈
	ZnO-TiO ₂ (rutile) solid reaction (800°C)	Zn ₂ TiO ₄ and ZnTiO ₃
Reddy et al. (1984)	Hydrolysis-pyrolysis of TiCl ₄ and ZnCl ₂ (700-900°C)	Zn ₂ TiO ₄ and Zn ₂ Ti ₃ O ₈

Table 2.2 Stable zinc titanate phases for Zn/Ti < 2 and temperatures below 1000°C (cont'd.).

<u>Literature Source</u>	<u>Preparation</u>	<u>Zinc Titanate Phase</u>
Lercher et al. (1984)	Hydrolysis-pyrolysis of TiCl_4 and ZnCl_2 (500°C)	ZnTiO_3
Yamaguchi et al. (1987)	Hydrolysis-pyrolysis of $\text{Ti}(\text{OC}_3\text{H}_7)_4$ and $\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2$	$\text{Zn}_2\text{Ti}_3\text{O}_8$ (600-765°C)
		$\text{Zn}_2\text{Ti}_3\text{O}_8 \rightarrow \text{ZnTiO}_3$ (820-965°C)
		$\text{ZnTiO}_3 \rightarrow \text{Zn}_2\text{TiO}_4$ (965-1010°C)
This work	Complexation with citric acid (600-720°C) $\text{Ti}(\text{OC}_3\text{H}_7)_4$ and $\text{Zn}(\text{CH}_3\text{CO}_2) \cdot 2\text{H}_2\text{O}$	Zn_2TiO_4 , ZnTiO_3 and $\text{Zn}_2\text{Ti}_3\text{O}_8$

$\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2$, they observed the following reactions:

This reaction scheme is in better agreement with the experimental results obtained in this study. At 1000°C , both ZnTiO_3 and $\text{Zn}_2\text{Ti}_3\text{O}_8$ were found to break into Zn_2TiO_4 and rutile TiO_2 . However, in this work, ZnTiO_3 was formed at temperatures below 820°C . Whether ZnTiO_3 or $\text{Zn}_2\text{Ti}_3\text{O}_8$ is formed depends to a large degree on the preparation conditions and titanium precursor. In most of the previous studies, either rutile or anatase TiO_2 was used. In those cases, either ZnTiO_3 or $\text{Zn}_2\text{Ti}_3\text{O}_8$ was formed exclusively. However, in this study, titanium (IV) i-propoxide was used which can yield both ZnTiO_3 and $\text{Zn}_2\text{Ti}_3\text{O}_8$. ZnTiO_3 is present at lower temperatures than 820°C because a complexation technique with citric acid was used. As discussed previously, because of the smaller diffusion length of the reactants, lower temperatures (than the hydrolysis-pyrolysis technique) can be used to form different phases. In this study, at 500°C , the solids were very microcrystalline with the formation of either $\text{Zn}_2\text{Ti}_3\text{O}_8$ and/or Zn_2TiO_4 . At 600°C , ZnTiO_3 is formed. The transformations observed here ($\text{Zn}_2\text{Ti}_3\text{O}_8$ and/or $\text{Zn}_2\text{TiO}_4 \rightarrow \text{ZnTiO}_3 \rightarrow \text{Zn}_2\text{TiO}_4 + \text{TiO}_2$) would be in agreement with Yamaguchi et al. (1987) if the low temperature (500°C) zinc titanate phase was $\text{Zn}_2\text{Ti}_3\text{O}_8$.

2.3.2 Physical Properties

The effects of mixed oxide compositions and calcination temperatures on the solid physical properties were determined. SEM micrographs of ZT (1 Zn:1 Ti) calcined from

500-800°C are shown in Figures 2.5-2.8. The surface area variations with temperature are shown in Figure 2.9 for ZT in addition to Z2T3, Z2T and ZnO. ZT calcined at 500°C is very microcrystalline (Figure 2.5). The average crystal size is between 0.01-0.08 μm with a corresponding surface area of 51.3 m²/g. At 600 and 700°C, there is no large change in the surface morphologies of the solids (Figure 2.6 and 2.7). The surface of these solids has higher zinc concentration than the bulk. Zn/Ti ratios of 1.5 were detected by EDS. The crystallinity of the solids increases with increasing calcination temperature with a corresponding drop in surface area (to 2.4 m²/g at 700°C). The largest change is observed in ZT calcined at 800°C (Figure 2.8). Large rod-shaped crystals are found on the surface. EDS analyses of these crystals find Zn/Ti=8.9. These crystals are believed to result from the reduction of zinc titanate and zinc oxide by carbon in the bulk of the solid to form Zn(g), according to the reactions:

whereupon Zn(g) diffuses out and reacts with O₂ to form ZnO crystals by:

Zinc titanates prepared by the amorphous citrate technique form a "skin" (or "crust") of low porosity. Figure 2.10 shows SEM micrographs of the solid Z3T calcined at 720°C for 12 h. In comparison to this "skin" (Figure 2.10a), the bulk of the solid (Figure 2.10b) is much more porous. The zinc titanate "skin" formation causes lower solid reactivity in sulfidation (Section 4). Since sulfidation is accompanied by the formation of a solid product of higher molar volume than the reactant, the reactivity decreases as the "skin" porosity is

a)

b)

Figure 2.5 SEM micrographs of ZT (1 Zn : 1 Ti) calcined at 500°C for 4 h a) 10000x and b) 20000x.

a)

b)

Figure 2.6 SEM micrographs of ZT (1 Zn : 1 Ti) calcined at 600°C for 4 h a) 10000x and b) 20000x.

a)

b)

Figure 2.7 SEM micrographs of ZT (1 Zn : 1 Ti) calcined at 700°C for 4 h a) 10000x and b) 20000x.

Figure 2.8 SEM micrographs of ZT (1 Zn : 1 Ti) calcined at 800°C for 4 h a) 5000x and b) 10000x.

Figure 2.9 Effect of calcination temperature on the Zn-Ti-O surface area.

a)

b)

Figure 2.10 SEM micrographs of Z3T (3 Zn : 1 Ti) calcined at 720°C for 12 h a) surface "skin" and b) porous bulk.

decreased. This effect can be lessened by crushing the solid to a small size. Another way to diminish the effect of the "skin" formation is by preparing a solid with a higher amount of citric acid. The evolution of large amounts of CO_2 and H_2O causes the formation of a more porous "skin." ZnO also formed a "skin." In contrast to Zn-Ti-O , however, this "skin" is very porous (Figure 2.11).

Typical pore size distributions are shown in Figure 2.12 for the solids Z3T and ZnO calcined at 720°C for 12 h with particle size in the range of 90-125 μm . Solids prepared by the amorphous citrate technique have characteristically large pores formed by the evolution of CO_2 and H_2O during the heating process. For Z3T, a bimodal pore size distribution is present. The pores are predominantly 12 μm (radius). There is also a smaller peak (approximately 10% to the total pore volume) with pores approximately 0.028 μm (radius). ZnO , however, is characterized by a unimodal pore size distribution. The center of the peak in the ZnO pore size distribution plot is approximately 6 μm (radius). The lower percentage ($< 1\%$) of smaller pores (ca. 0.028 μm) in ZnO is consistent with the lower surface area of ZnO ($1.3 \text{ m}^2/\text{g}$) compared to Z3T ($7.6 \text{ m}^2/\text{g}$).

The effect of Zn/Ti ratio on the solid surface area and pore volume is shown in Figures 2.13 and 2.14, respectively. These solids were calcined at 720°C for 12 h. The presence of titanium in the solids can yield higher surface area than pure ZnO . Maxima in the surface area and pore volume profiles are found at $\text{Zn/Ti} \approx 9$. Figure 2.9 also shows similarly high surface for Zn-Ti mixed oxides at various temperatures. At 500°C , the surface area of Zn-Ti mixed oxides with Zn/Ti ratio ranging from 2/3 to 2/1 is in the range of $73\text{-}56 \text{ m}^2/\text{g}$, while for ZnO it is only $7 \text{ m}^2/\text{g}$. Thus, TiO_2 addition into ZnO suppresses

a)

b)

Figure 2.11 SEM micrographs of ZnO calcined at 720°C for 12 h.

Figure 2.12 Pore size distributions of Z3T (3 Zn:1 Ti) and ZnO calcined at 720°C for 12 h.

Figure 2.13 Effect of Zn-Ti composition on the surface area.

Figure 2.14 Effect of Zn-Ti composition on the pore volume.

the grain growth of the latter. Inhibition of grain growth by second solid phase inclusion has been observed by others. Weyl (1952) observed that lithium oxide decreases the rate of ZnO sintering while aluminum oxide increases it. Gupta (1971) found that potassium oxide decreases the rate of ZnO sintering.

2.4 CONCLUSIONS

1. Three zinc titanate phases (Zn_2TiO_4 , ZnTiO_3 , $\text{Zn}_2\text{Ti}_3\text{O}_8$) can be formed through solids preparation by the complexation method with citric acid using zinc acetate and titanium (IV) iso-propoxide precursors followed by pyrolysis at different time-temperature conditions.

2. The observed phase transformation with increasing temperature is: $\text{Zn}_2\text{Ti}_3\text{O}_8 \rightarrow \text{ZnTiO}_3 \rightarrow \text{Zn}_2\text{TiO}_4$.

3. Zn_2TiO_4 is the stable phase for all Zn-Ti-O solids calcined at temperatures $\geq 1000^\circ\text{C}$ or for solids with $\text{Zn/Ti} \geq 2$ calcined at temperatures $\geq 700^\circ\text{C}$ and for long periods of time (≥ 12 h). At temperatures below 800°C , all three phases ($\text{Zn}_2\text{Ti}_3\text{O}_8$, ZnTiO_3 , Zn_2TiO_4) may be present.

4. Zn-Ti mixed oxides (with up to 50 mol% TiO_2) are characterized by higher surface area and pore volume than ZnO neat.

3. REDUCTION OF ZN-TI-O MATERIALS

3.1 BACKGROUND

The reduction of ZnO by carbon monoxide and hydrogen gas has been the subject of many studies over the years. Some of the earlier investigators (Bodenstein, 1927; Maier and Ralston, 1928) were mainly interested in the extraction of zinc from ores in a retort furnace by the reaction:

Subsequently, the carbon monoxide formed can itself reduce ZnO by:

These early studies, however, were performed at near equilibrium conditions.

More recent investigations (discussed below) examined the reaction of ZnO with H_2 as well as CO under non-equilibrium conditions to determine kinetic parameters of the reaction. Because the reduction reaction is highly reversible, various methods were used to ensure that gas diffusion was not rate determining and that the reaction rate was not at equilibrium. The equilibrium constants at various temperatures for the reduction of ZnO and Zn_2TiO_4 with H_2 are shown in Figure 3.1 (Barin and Knacke, 1973; Barin et al., 1976). Typically, the equilibrium constants are small (*ca.* 10^{-2}) with $\Delta G > 0$.

Several studies (Truesdale and Waring, 1944; Guger and Manning, 1971; Gioia et al., 1977) used sintered ZnO pellets to investigate the reaction. Hegedus and Kiss (1966) used ZnO powders in their studies. Grunze and Hirschwald (1974; 1975) studied the reaction of powders, sintered samples, and single crystals at low pressure (0.01-10 Torr). The low

Figure 3.1 Equilibrium constants for ZnO and Zn₂TiO₄ reduction with hydrogen gas.
(Barin and Knacke, 1973; Barin et al., 1976)

pressure served to eliminate as much as possible any diffusional effects. Table 3.1 lists the experimental conditions and activation energies reported in the literature for the reduction of ZnO with H₂ and CO. These experiments were performed in the temperature range of 350-1500°C. ZnO reduction by H₂ has been detected at temperatures as low as 160°C (Bonasewicz et al., 1981). From the similarity in the activation energies for both reduction in H₂ and CO, it was concluded that the same reduction mechanism is present in reaction with both gases (Grunze and Hirschwald, 1975). However, the frequency factor of the rate constant for reduction of ZnO with H₂ is approximately twice as large as that with CO. At higher pressures, Grunze and Hirschwald (1974; 1975) observed increasing activation energies. As the temperature increased and the pressure decreased, the reaction order increased from 0.25 to 1. Interesting results were obtained with different types of samples. Reduction of zinc oxide single crystals gave lower activation energies than powders. Grunze and Hirschwald (1975) hypothesized that in porous powders, removal of the products is hindered. Part of the enthalpy of reaction is included in the experimental activation energies. Consequently, higher activation energies are observed.

The presence of water vapor significantly affected the reduction of ZnO. Through thermogravimetric studies, Hegedus and Kiss (1966) observed that as the water vapor content in a flowing stream of hydrogen increased from $7.0 \times 10^{-3}\%$ (0.053 Torr) to $5.9 \times 10^{-2}\%$ (0.45 Torr), the activation energy for reduction increased from 27.4 kcal/mol to 52 kcal/mol. Correspondingly, as the amount of water vapor was increased, the reduction rate decreased. However, when the amount of H₂O was increased further to 2.1% (16.2 Torr), no further change in the activation energy was observed. Flytzani-Stephanopoulos et al. (1987) also

Table 3.1 Apparent activation energies and experimental conditions reported in the literature for ZnO reduction with (A) CO and (B) H₂.¹

Reference	Pressure (Torr)	Temperature (°C)	Apparent Activation Energy (kcal/mol)		
			Powders	Sintered samples	Single crystals
Truesdale and Waring (1944)	760	750-1100		A: 20-25 B: 20-25	
Hegedus and Kiss (1966)	760	450-640	B: 27		
Guger and Manning (1971)	760	1000-1500		A: 38	
Gioia et al. (1977)	760	770-970		B: 29	
Grunze and Hirschwald (1974; 1975)	10 ⁻¹ -10 ⁻²	500-700	A: 28		
	10 ⁻² -8	415-800		A: 13-31	
	10 ⁻² -4	500-800		B: 19-29	
Gast et al. (1976)	10 ⁻² -10 ⁻¹				A: (0001): 14 A: (0001): 17 A: (1010): 16
This work	760	550-1050	B:24		

¹ modified table from Grunze (1981)

observed lower zinc oxide as well as zinc titanate reduction rates in the presence of H_2O vapor.

The first study of the reduction of Zn-Ti-O materials was reported by Flytzani-Stephanopoulos et al. (1987). A lower reduction rate by as much as five times was reported for Zn-Ti-O solids compared to ZnO. However, these experiments were carried out in a fixed bed reactor where mass transfer resistance may have been limiting. It has been reported by Hirschwald and Noack (1972) that it is possible to decrease the reducibility of ZnO by the inclusion of small amount of foreign atoms. They found that the reduction of ZnO can be inhibited by the addition of small amount (1 mol%) of Li_2O , Al_2O_3 , or Ga_2O_3 . They attributed this to a change in the electronic state of zinc oxide. However, no such information exists for TiO_2 addition into ZnO.

A major objective of this project was to determine whether Zn-Ti-O materials are intrinsically more resistive to reduction than ZnO and to determine the composition of Zn-Ti-O needed to yield the lowest reduction rate. The mechanisms and kinetics of the reduction of Zn-Ti-O solids were studied and compared with ZnO reduction to elucidate the role of titanium in reduction. Only reduction by hydrogen was investigated. Based on earlier studies (Grunze and Hirschwald, 1974), reduction of ZnO in H_2 is faster than in CO. Thus, the reduction rates obtained with H_2 represent the maximum amount of zinc loss possible in a coal gas atmosphere. The effect of H_2O on the rate of reduction was examined since H_2O is a major component in coal gases, and, as discussed above, it has been observed by others to have an inhibitory effect on the reduction of ZnO. The effect of H_2S on reduction was also investigated.

3.2 EXPERIMENTAL METHODS

Reduction experiments with solids containing various Zn/Ti atomic ratios were performed. The preparation and characterization of the solids were discussed in Section 2. The analytical techniques included BET-N₂ for surface area measurements, scanning electron microscopy (SEM) coupled with energy dispersive X-ray (EDS) analysis for surface morphology and elemental distribution determination, and X-ray diffraction (XRD) for crystalline phase identification. To ensure that rate measurements were performed in the absence of gas phase diffusion limitation or equilibrium limitation, small amounts (1-2 mg) of material was used in each test and several samples were sintered at 1000°C for 1 h to reduce their surface area. The chemical and physical properties of solids used in the reduction experiments are shown in Table 3.2.

Kinetic experiments were performed in a Cahn System 113-X thermogravimetric analyzer (TGA) equipped with a Cahn 2000 electrobalance, a Micricon temperature controller, and a Bascom Turner data acquisition system. The TGA measured the weight loss as a function of the time required for ZnO reduction to Zn followed by rapid zinc vaporization.

The reactant gas containing various concentrations of H₂, H₂O vapor, and N₂ was introduced into the apparatus through a side arm (Figure 3.2). Gas flow rates were set by passing H₂ and N₂ gases through Brooks Model 5850E mass flow controllers. A gas flow rate of 485 sccm was used in the experiments. Water vapor was added to the gas by bubbling nitrogen and hydrogen through a water saturator maintained at either 25°C or 51°C in a three-neck flask assembly. The saturated gas stream entered the apparatus side

Table 3.2 Chemical and Physical Properties of Sorbents¹

Sorbent	(Zn/Ti) (atomic ratio)	Calcination Temperature ² (°C)	Surface Area (m ² /g)	Crystalline Phases (wt %)				
				ZnO	Zn ₂ TiO ₄	Zn ₂ Ti ₃ O ₈	ZnTiO ₃	TiO ₂
ZnO	---	1000, 1 h	0.68	100	0	0	0	0
Z9T	9/1	1000, 1 h	1.03	70	30	0	0	0
Z3T	3/1	1000, 1 h	0.94	25	75	0	0	0
Z2T	2/1	1000, 1 h	0.76	0	100	0	0	0
Z3T2	3/2	720, 12 h	2.18	0	68	14	18	0
ZT-a	1/1	1000, 1 h	0.40	0	75	0	0	25
ZT-b	1/1	720, 12 h	1.64	0	20	35	45	0
Z2T3-a	2/3	720, 12 h	2.29	0	0	16	65	19
Z2T3-b	2/3	700, 12 h ³	1.30	0	0	0	83	17

¹ Reduction experiments performed with 90-125 µm particles² Sorbents calcined at 1000°C were first calcined at 720°C for 12 h³ Calcined in the absence of air flow (static conditions)

Figure 3.2 Schematic of the thermobalance reactor system.

arm through heated lines. A thin layer of sample (ca. 1 mg and 90-125 μm size particles) was placed on a quartz pan suspended by a quartz hangdown wire. Isothermal reduction experiments were performed at temperatures between 550-1050°C. The sample was pretreated in a vacuum oven at 90°C for 1 h to remove any absorbed H_2O before it was reacted in the TGA.

It was not possible to directly examine the effect of hydrogen sulfide on reduction since in addition to reduction, sulfidation would also occur. To separate these effects, the solids were first partially sulfided (10-15%) in 2 mol% H_2S -1 mol% H_2 -97 mol% N_2 and then reduced in 10 mol% H_2 -90 mol% N_2 . Sulfidation and reduction were performed at the same temperature.

3.3 PRESENTATION AND DISCUSSION OF REDUCTION RESULTS

3.3.1 Initial Reduction Rate of Bulk Zn-Ti-O Sorbents: Hydrogen-Nitrogen Mixtures

Initial rate experiments in the TGA were performed under isothermal conditions to determine the reduction reactivity of solids containing various atomic ratios of Zn:Ti and various chemical phases (e.g. ZnO , Zn_2TiO_4 , ZnTiO_3 , and $\text{Zn}_2\text{Ti}_3\text{O}_8$). Kinetic parameters (e.g. activation energies) were determined from these experiments. The possible overall reduction reactions are:

At 1300 K, the K_{eq} for reaction (3.8) is 3.4×10^{-3} for the rutile form of TiO_2 . Although this value is small, reduction of TiO_2 is possible. To check whether there was any reduction of TiO_2 , both rutile (UCI 1090-113 extrusions crushed to 90-125 μm size particles) as well as anatase (obtained from Aldrich Chemical Co.) were reacted with H_2 at 700-1000°C. The reduction of TiO_2 in hydrogen at elevated temperature can be observed by a change in color from white to bluish gray (Matsuda and Kato, 1983) due to the formation of Ti_3O_5 . No weight change of either crystalline form of TiO_2 was observed after 60 minutes in 10 mol% H_2 -90 mol% N_2 at each temperature of 700, 800 or 1000°C. The color of TiO_2 was changed to gray only after the experiment at 1000°C indicating that surface reduction of TiO_2 took place under these conditions.

In addition to the above overall reduction reactions, there is the possibility of zinc loss by dissociative vaporization of ZnO according to the reactions:

However, reaction (3.9) becomes significant only above 1300-1400°C (Hirschwald and Stolze, 1971). At 1300°C, the experimentally measured vapor pressure is only about 1 Torr. Several other investigators (Moore and Williams, 1959; Secco, 1960) have reported rapid vaporization of ZnO in a zinc vapor atmosphere at temperatures below 1300°C. However, Koder et al. (1968) found that the apparently accelerated vaporization rates were due to the presence of carbonaceous impurities which reacted with ZnO to produce CO . Subsequently, CO reacted with ZnO . Most of the Zn - Ti - O materials used in this study were calcined at 1000°C. This ensured that no residual carbon was present in the samples.

However, it was necessary to also have some Zn-Ti-O materials calcined at only 720°C to obtain reduction rate measurements for different zinc titanate phases.

The rate of zinc loss was measured at temperatures between 550-1050°C in various concentrations of hydrogen. It was assumed that this measured rate represents the rate of reduction. In this temperature range, zinc can exist either in a liquid or gas phase. At temperatures below 420°C, zinc exists in the solid phase. Between 420-911°C, zinc exists in the liquid phase (Barin and Knacke, 1973; Barin et al., 1976). Above 911°C, only gaseous zinc is formed. Although at 550°C liquid zinc is formed, its vapor pressure (5.92 Torr) is high enough that it will completely evaporate. Thus, at temperatures below 911°C, the reactions for ZnO reduction are:

To determine whether the assumption that the rate of zinc evaporation (Eq. 3.12) is relatively rapid compared to the rate of reduction (Eq. 3.11), the rate of evaporation was calculated. Assuming reaction (3.11) is much faster than reaction (3.12), at 550°C with a gas flowrate of 485 sccm, the calculated rate of zinc loss is 3×10^{-6} mol Zn/s. In contrast, the measured rate of zinc loss of ZnO (calcined at 1000°C) in 10 mol% H₂-90 mol% N₂ at 550°C was approximately three orders of magnitude smaller. Consequently, the rate determining step is the reduction reaction (Eq. 3.11).

Reactions 3.4 and 3.5 are endothermic. At 1300 K, the heat of reaction for (3.4) is 51400 cal/mol and for reaction (3.5) is 51100 cal/mol (Barin and Knacke, 1973; Barin et al., 1976). Thermodynamic data were not available for ZnTiO₃ or Zn₂Ti₃O₈. With the

relatively high heats of reaction, there is some concern about possible cooling effects. A simple estimate of the maximum possible temperature drop using known methods discussed in Smith (1970) was made. At 1300 K, the calculated decrease in temperature across the gas film is only 1.8°C for ZnO in a gas containing 10 mol% H₂-90 mol% N₂. Thus, the isothermal assumption is valid for these experiments.

The initial reduction rate of various Zn-Ti-O materials listed in Table 3.2 was measured in 10 mol% H₂-90 mol% N₂. The initial rate was calculated by:

$$R_o = \frac{(dW/dt)_{t=0}}{(81.3794) A_o} \quad (3.13)$$

where the initial rate R_o [=] mmol cm⁻² s⁻¹, $(dW/dt)_{t=0}$ [=] mg/s is the slope of the weight vs. time profile at $t=0$, 81.3794 is the molecular weight of ZnO, and A_o [=] cm² is the initial surface area of the reactant solid. Comparative plots of the initial reduction rates of solids containing various Zn:Ti atomic ratios reacted at 600 and 700°C are shown in Figure 3.3. At both 600 and 700°C, the rate of reduction of ZnO was greater than that of any of the Zn-Ti-O solids. With as little as 10 mol% TiO₂ (sorbent Z9T), there was still a significant (twofold) decrease in the rate of ZnO reduction. The reduction rate of ZnO was about 13 times greater than Zn-Ti-O solids with $(Zn/Ti)_{\text{atomic ratio}} \leq 3$ at 600°C and ten times greater at 700°C. When the relative amount of TiO₂ was increased above 25 mol%, no significant change in the reduction rate was observed. This implied that the presence of different zinc titanate phases had no significant effect on reduction. For example, the solid Z2T (2 Zn : 1 Ti) which contained only the crystalline phase Zn₂TiO₄ had approximately the same reduction rate as the solid Z2T3-b, which contained a mixture of ZnTiO₃ and TiO₂. Also

Figure 3.3 Comparative plots of the initial reduction rate of various Zn-Ti-O materials reacted at 600 and 700°C in 10% H₂-90% N₂.

the sorbents Z2T3-a (containing $\text{Zn}_2\text{Ti}_3\text{O}_8$, ZnTiO_3 and TiO_2) and Z2T3-b (containing ZnTiO_3 and TiO_2) gave similar initial reduction rates. This finding simplified testing because it eliminated the need to prepare pure zinc titanate phases of the type $\text{Zn}_2\text{Ti}_3\text{O}_8$ or ZnTiO_3 , which were hard to obtain. Often mixtures of these phases were formed.

In order to elucidate the mechanism by which the presence of titanium in the solid inhibits the reduction reaction, further kinetic experiments were performed. In the absence of both diffusional and mass transfer resistances, an intrinsic initial heterogeneous rate expression of the form

$$R_o = k C_{\text{H}_2}^n \quad (3.14)$$

was used, where k is the intrinsic rate constant, C_{H_2} mmol/cm³ is the molar concentration of hydrogen gas, and n is the reaction order. The reaction order of ZnO and Z2T reduction was determined by varying the hydrogen gas concentration at 700°C as shown in Figure 3.4. From these results, the reaction orders for ZnO and Z2T reduction with hydrogen were determined with the equation

$$\ln R_o = \ln k + n \ln C_{\text{H}_2} \quad (3.15)$$

For ZnO, at 700°C the reaction order is 0.51 ± 0.05 while that of Z2T is 1. The former result is in agreement with the work of Grunze and Hirschwald (1974; 1975). These authors observed fractional reaction orders for ZnO reduction. At pressures in the range of 1-4 Torr, they found that the reaction order decreased from 0.77 at 800°C to 0.25 at 428°C. At 700°C, they reported a reaction order of 0.60. This is close to the value reported in this study. The somewhat smaller reaction order in this study is probably due to the higher reaction pressure (760 Torr). To confirm that there existed a dependence of the apparent

Figure 3.4 Effect of hydrogen concentration on the initial rate of reduction of ZnO and Z2T at 700 C.

Figure 3.5 Effect of hydrogen concentration on the initial reduction of ZnO at various temperatures.

reaction order on the reduction temperature for ZnO, the reaction orders at several different temperatures were measured. The results are shown in Figure 3.5. The apparent reaction order increased somewhat from approximately 0.42 at 600°C to 0.59 at 900°C. This was consistent with a Langmuir-Hinshelwood expression:

$$R_o = \frac{KC_{H_2}}{(1 + \sqrt{K_{H_2}C_{H_2}})^2} \quad (3.16)$$

where K is a term which depends on the rate controlling step (e.g. $K = k_r K_{H_2}$ when the surface reaction is controlling; k_r is the rate constant of the surface reaction) and K_{H_2} is the hydrogen adsorption equilibrium constant. An adsorption process is almost always exothermic. Thus, K_{H_2} decreases exponentially with increasing temperature by a factor of $e^{\lambda/RT}$ where λ (>0) is the heat of chemisorption. Consequently, as the temperature increases, the apparent reaction order increases to 1.

The reaction rate constant can be expressed using an Arrhenius relationship, thus defining an activation energy:

$$k_r = k_o \exp (-E/RT) \quad (3.17)$$

where k_o [=] $\text{mmol}^{1-n}/\text{cm}^{-3n+2}/\text{s}$ is a constant, E is the activation energy, R is the ideal gas constant, and T is the absolute temperature. Because of the difference in reaction order between ZnO and Z2T it is not possible to directly compare the Arrhenius plots of ZnO and Z2T. To facilitate the comparison of ZnO and Z2T, Arrhenius-type plots are drawn in terms of initial rate versus $1/T$. However, the activation energy and k_o were calculated by Equation 3.17. Figure 3.6 shows the initial reduction rates of ZnO and Z2T on Arrhenius plots. At all temperatures (550-1050°C), the rate of reduction of ZnO was faster

Figure 3.6 Arrhenius plots of the initial reduction rates of ZnO and Z2T.

Figure 3.7 Arrhenius plots of the initial reduction rates for various Zn-Ti-O solids.

than Z2T. Based on Equation 3.17, an activation energy of 24 kcal/mol and k_0 of $27.5 \text{ mmol}^{0.49} \text{ cm}^{-0.47} \text{ s}^{-1}$ were obtained for reduction in 10 mol% H_2 -90 mol% N_2 . This activation energy was close to the values reported by others (Table 3.1). The reported values of the activation energy were 27-28 kcal/mol for ZnO powders. For Z2T, the activation energy was 37.3 kcal/mol and k_0 was $6.3 \times 10^4 \text{ cm/s}$.

Figure 3.7 shows that the initial reduction rates of various Zn-Ti-O materials with $(\text{Zn/Ti})_{\text{atomic}} \leq 3$ are similar to that of the sorbent Z2T. The solid Z9T, on the other hand, behaves like ZnO. Figure 3.8 shows the Arrhenius plots of the initial reduction rates of ZnO and Z9T. The activation energy for Z9T was 24.7 kcal/mol, similar to the value obtained for ZnO. This indicated that the same reaction mechanism was involved in the reduction of ZnO and Z9T. This was not surprising considering that Z9T contains 70 wt% ZnO as well as 30 wt% Zn_2TiO_4 present as crystalline phases. The major difference between ZnO and Z9T was the constant k_0 . For ZnO, k_0 was $27.7 \text{ mmol}^{0.49} \text{ cm}^{-0.47} \text{ s}^{-1}$, while for Z9T it was $17.4 \text{ mmol}^{0.49} \text{ cm}^{-0.47} \text{ s}^{-1}$.

3.3.2 Initial Reduction Rate of Bulk Zn-Ti-O Sorbents: Effect of Water Vapor

Various amounts of water vapor were added to the reducing gas to determine if any inhibitory effect on the reduction rate was present. For ZnO, a dramatic effect of H_2O on reduction was observed. Figure 3.9 shows the Arrhenius plots of ZnO reduction in the presence of various amounts of water vapor. The inclusion of 1 mol% H_2O in the gas significantly decreased the reduction rate of ZnO. However, when the amount of water vapor was increased to 3 or 8 mol%, the reduction rate did not decrease any more. The activation energy was significantly higher in the presence of water vapor. With a gas con-

Figure 3.8 Arrhenius plots of the initial reduction rates of ZnO and Z9T.

Figure 3.9 Arrhenius plots of the initial reduction rates of ZnO in the presence of various amounts of H₂O vapor.

Figure 3.10 Arrhenius plots of the initial reduction rates of Z2T in the presence of various amounts of H₂O vapor.

taining 10 mol% H₂-3 mol% H₂O-87 mol% N₂, the activation energy was 43.9 kcal/mol and k_0 was 9.27×10^5 cm/s. In contrast, the activation energy was only 24.0 kcal/mol for dry reduction.

H₂O also had an inhibitory effect on the reduction of Zn-Ti-O solids. Figure 3.10 shows the Arrhenius plots of Z2T reduction in the presence of 0, 3 and 8 mol% H₂O. However, water vapor affected the reduction kinetics of Z2T less than that of ZnO. The activation energy increased from 37.3 to 44.0 kcal/mol and k_0 changed to 3.36×10^5 cm/s. The new activation energy was approximately the same as the value obtained for ZnO reduction (43.9 kcal/mol) in the presence of 3 mol% H₂O. The only difference was that the pre-exponential factor, k_0 , for Z2T was 2.8 times smaller than that of ZnO. No effect on the reduction of Z2T was observed when a gas mixture with higher H₂O content (8 mol%) was used, similar to the results for ZnO.

For ZnO, there was a concomitant change in the reaction order in the presence of water vapor. Figure 3.11 shows the effect of hydrogen concentration on the initial reduction rate of ZnO and Z2T in the presence of 3 mol% H₂O at 700°C. The reaction order for ZnO changed to 1 from its value of 0.51 in the absence of H₂O. In contrast, the reaction rate of Z2T remained first order. As discussed in Section 3.1, similar inhibitory effects on ZnO reduction by water vapor have been observed by others (Hegedus and Kiss, 1966; Flytzani-Stephanopoulos et al., 1987).

A comparative plot of the initial reduction rates of various Zn-Ti-O materials at 700°C in 10 mol% H₂-3 mol% H₂O-87 mol% N₂ is shown in Figure 3.12. The reduction rates of Zn-Ti-O solids were lower than for bulk ZnO. The reduction rate steadily

Figure 3.11 Effect of hydrogen concentration on the initial reduction rate of ZnO and Z2T in the presence of 3% H₂O at 700°C.

Figure 3.12 A comparative plot of the initial reduction rates of various Zn-Ti-O materials reacted at 700°C in 10%H₂-3%H₂O-87%N₂.

decreased as the relative amount of TiO_2 in the solid was increased. Unlike the dry reduction results (Figure 3.3), no plateau is shown in Figure 3.12 for solids with $(\text{Zn}/\text{Ti})_{\text{atomic}} \leq 3$. Comparative Arrhenius plots of ZnO, Z2T and Z2T3-b in the presence of H_2O are shown in Figure 3.13. The activation energies of all solids were approximately the same (ca. 44 kcal/mol). The difference in reactivity lies in the pre-exponential constant, k_0 , as listed in Table 3.3. For Z2T3-b, the value of k_0 was 7.1 times smaller than for ZnO.

In an earlier paper (Lew et al., 1989) dry reduction of higher surface area solids (e.g. ZnO :2.4 m^2/g) was reported to occur at rates lower (by tenfold) than that in this work. The self-inhibitory effect produced by the larger product H_2O concentrations in the earlier study can explain the lower reported values of reduction rates. Hegedus and Kiss (1966) observed a decrease in the reduction rate as the mole fraction of H_2O was varied from 7.0×10^{-3} to 5.9×10^{-2} %. In our previous work, the product H_2O mole fraction was 6.5×10^{-3} % based on

Table 3.3 Values of k_0 for solid reduction in the presence of H_2O ¹

	$k_0(\text{cm/s})$
ZnO	9.27×10^5
Z2T	3.36×10^5
Z2T3-b	1.31×10^5

¹Arrhenius plots shown in Figure 3.13.

Figure 3.13 Arrhenius plots of the initial reduction rates of ZnO, Z2T and Z2T3 in 10%H₂-3%H₂O-87%N₂.

the rate of H_2O production and the gas flowrate, while in the present paper, the conditions of Figure 3.3 correspond to H_2O content of 1.3×10^{-3} mol %. In addition higher water vapor pressure may be found in porous materials of high surface area where small pores are prevalent. Reduction experiments in $\text{H}_2\text{-N}_2$ performed in this laboratory with ZnO single crystals characterized by low surface area ($8.2 \times 10^{-4} \text{ m}^2/\text{g}$) and zero porosity yielded similar initial reduction rate to the low-surface area ($0.68 \text{ m}^2/\text{g}$) bulk ZnO solid reported here.

3.3.3 Initial Reduction Rate of Bulk Zn-Ti-O Sorbents: Effect of Partial Sulfidation

ZnO and Z2T were sulfided 10-15% between 600 and 700°C. Reduction of the partially sulfided solids in 10 mol% H_2 -90 mol% N_2 showed a lower initial reduction rate than reduction of the unsulfided solids. In these experiments, only the oxides were reduced. No reduction of ZnS was observed by measuring the weight change. As shown in Figure 3.14, there appeared to be a similar inhibitory effect on reduction by hydrogen sulfide as was found with water vapor. Figure 3.14b shows the reduction profiles. A sigmoidal shape profile is found for ZnO which has been partially sulfided. Initially (<10min) the reduction profiles of ZnO partially sulfided and the profile of ZnO reduced in the presence of 3% H_2O virtually overlap. As the reactant surface recedes from the sulfided layer, sites which are more reactive are exposed and a corresponding increase in rate is observed. The initial rates shown in Figure 3.14a were measured from the early part of the reduction profiles. Because of some contribution from the more reactive sites and the small change in weight, the initial rate measurements for the partially sulfided solid tend to be on the high side and have some degree of error. In the following section, a reduction model including the role

a)

b)

Figure 3.14 Reduction of partially sulfided solid a) comparison of the Arrhenius plots of the initial rate and b) comparison of reduction profiles.

of water vapor will be discussed. Hydrogen sulfide appears to play a role similar to that of water vapor.

3.3.4 Reduction Model

From the kinetic measurements described in the above section, a mechanism for ZnO reduction and inhibition by titanium dioxide can be proposed. For bulk ZnO, the inhibition pattern observed with water vapor suggests that two very different types of reaction sites are involved in reduction. The existence of multiple types of hydrogen chemisorption sites on the surface of ZnO at low temperatures ($<250^{\circ}\text{C}$) has been reported in the literature (Kesavulu and Taylor, 1960; Eischens et al., 1962; Dent and Kokes, 1969; Boccuzzi et al., 1978). Since the experiments performed in this project all took place at much higher temperatures ($\geq 550^{\circ}\text{C}$) than the earlier chemisorption studies, it was not possible to directly extend the knowledge gained from those studies to the analysis of this system. However, the mechanistic insights gained from the previous work on H_2 adsorption and H_2O effects on different ZnO sites are also employed here.

For ZnO reduction at $550\text{-}1050^{\circ}\text{C}$, two reaction sites are proposed. One type of sites, called type A, is characterized by a rapid reduction rate but is poisoned by water vapor. The other type of sites, called type B, has a slower reaction rate but is unaffected by H_2O . Since no change in the reduction rate is observed after a single monolayer has been reacted, it is assumed that the relative concentration of each type of sites is conserved in the successive monolayers. Each type of sites can be expressed in terms of a Langmuir-Hinshelwood equation. For type A sites, the following expression is obtained:

$$R_{o,A} = \frac{K_A C_{H_2}}{(1 + \sqrt{K_{H_2,A} C_{H_2}} + \sqrt{K_{H_2O,A} C_{H_2O}})^2} \quad (3.18)$$

where K_A is a constant related to the rate controlling step for the reaction, $K_{H_2,A}$ and $K_{H_2O,A}$ are the hydrogen and water adsorption equilibrium constants on type A sites, respectively. From the apparent reaction order of ZnO reduction in the absence of H_2O ($n = ca. 0.51$ at $700^\circ C$), $(K_{H_2,A} C_{H_2})^{0.5}$ must be the same order of magnitude as 1. In the presence of H_2O , sites A are poisoned. This is equivalent to $(K_{H_2O,A} C_{H_2O})^{0.5} \gg 1$ or $(K_{H_2,A} C_{H_2})^{0.5}$. Thus, $R_{o,A}$ becomes small. For type B sites, a similar Langmuir-Hinshelwood equation is obtained

$$R_{o,B} = \frac{K_B C_{H_2}}{(1 + \sqrt{K_{H_2,B} C_{H_2}} + \sqrt{K_{H_2O,B} C_{H_2O}})^2} \quad (3.19)$$

However, since the apparent reaction order of ZnO reduction in the presence of H_2O was unity and there was no significant effect on the reduction rate when the amount of H_2O was increased from 1 to 8 mol%, then $(K_{H_2,B} C_{H_2})^{0.5}$ and $(K_{H_2O,B} C_{H_2O})^{0.5} \ll 1$. Consequently, Eq. 3.19 reduces to

$$R_{o,B} = K_B C_{H_2} \quad (3.20)$$

The reaction rate is equal to the sum of the reactions on type A and B sites:

$$R_o = R_{o,A} + R_{o,B} \quad (3.21)$$

In the absence of H_2O , reaction on type A sites is much faster than on type B sites. Thus, $R_o = R_{o,A}$. At $700^\circ C$ from the initial rates obtained at various hydrogen concentrations, the

values of the constants are calculated and Eq. (3.18) becomes:

$$R_{o,A} = \frac{(1.27 \times 10^{-2} [\text{cm/s}]) C_{H_2}}{(1 + \sqrt{509.0 [\text{cm}^3/\text{mmol}] C_{H_2}})^2} \quad (3.22)$$

In the presence of H_2O , $R_{o,A} \approx 0$ and $R_o \approx R_{o,B}$. For ZnO with the experimental results obtained with 10 mol% H_2 -3 mol% H_2O -87 mol% N_2 , Eq. (3.20) becomes:

$$R_{o,B} = 9.27 \times 10^5 [\text{cm/s}] e^{-43.9 [\text{kcal/mol}]/RT} C_{H_2} \quad (3.23)$$

For Zn-Ti-O solids, the presence of titanium appears to either eliminate type A sites or modify their reactivity. The tenfold drop of the ZnO reduction rate in solids with $(\text{Zn/Ti})_{\text{atomic}} \leq 3$ at 700°C implies that type A sites are very sensitive to the presence of titanium. A solid (i.e. Z9T) with only 10 mol% TiO_2 (based on ZnO- TiO_2 stoichiometry) has a reduction rate 1.7 times slower than the reduction rate of ZnO in the absence of H_2O . Because the activation energy for Z9T reduction is the same as for ZnO and only the pre-exponential factor is different, this suggests that titanium eliminates type A sites. Thus, titanium has a geometric effect on the reduction kinetics of ZnO rather than an electronic effect. If there is a simple linear relationship between the relative amount of titanium and the number of type A sites eliminated, based on the observed reduction rate of Z9T, all type A sites can be eliminated in a solid containing 24.3 mol% TiO_2 . Experimentally, no further decrease of the reduction rate was observed when the relative amount of titanium was above 25 mol%. Reduction of solids with $(\text{Zn/Ti})_{\text{atomic}} \leq 3$, therefore, probably proceeds on another type of sites, labelled A', which is not affected by the presence of titanium or the type of zinc titanate compound formed. Similar to A sites, however, A' sites are also

poisoned by H₂O.

For Zn-Ti-O solids, in the absence of H₂O, the rate expression (3.18) for type A' sites becomes:

$$R_o = 6.30 \times 10^4 [cm/s] e^{-37.3[kcal/mol]/RT} C_{H_2} \quad (3.24)$$

In the presence of H₂O, both type A and A' sites are poisoned and reduction of Zn-Ti-O solids occurs by type B sites. This conclusion is drawn because of the similar values of the activation energies of Zn-Ti-O and ZnO solids. The effect of titanium is to decrease the pre-exponential factor in the rate expression. As shown in Figure 3.12, the reduction rate continued to decrease as the amount of titanium dioxide was increased from 0 to 60 mol%. Thus, the same rate expression as Eq. (3.23) is found for the reduction of Zn-Ti-O solids in the presence of water vapor. However, the pre-exponential factor decreases as the amount of titanium dioxide in the solid increases. This is very different from the situation without H₂O (Figure 3.3), indicating that type B sites are much less sensitive to the presence of titanium than type A sites. Consequently, a higher relative amount of titanium is needed to obtain lower reduction rates. The difference in sensitivity between sites A, A' and B may be explained geometrically by hypothesizing that type A sites are composed of groups or ensembles of atoms. Earlier studies have reported a type of sites for H₂ adsorption on ZnO consisting of a cluster of adjacent zinc cations and one oxygen anion (Boccuzzi et al., 1978; Griffin and Yates, 1982). The presence of titanium atoms in the cluster eliminates the activity of the site. The effect of titanium would be greatest on sites requiring the greatest number of nearby atoms. Consequently, type A' and B sites must be composed of fewer atoms than type A sites.

3.3.5 Reduction Conversion Profiles of Bulk Zn-Ti-O Solids

Typical experimental conversion-time profiles for ZnO and Z2T at 650 and 700°C are shown in Figures 3.15 and 3.16 (square symbols), respectively. The fractional conversion is defined as follows:

$$X = (W_i - W) / (W_i - W_f^I) \quad (3.25)$$

where W is the weight, W_i is the initial weight, and W_f^I is the final weight at complete conversion. For ZnO, W_f^I is equal to zero. W_f^I is the weight of the remaining TiO_2 for Zn-Ti-O solids. For both ZnO and Z2T, the reaction rates remained relatively constant up to a high level of conversion. At approximately 0.8-0.9 conversion, the reaction rate decreased. The experimental conversion profiles can be adequately described by the heterogeneous, gas-solid reaction of shrinking, nonporous spherical grains. In contrast, as discussed in Section 5, a discrete bimodal grain size distribution was needed to describe sulfidation of Z2T. The different requirements are found because during reduction the thick "skin" of low porosity breaks up into smaller pieces due to the escape of Zn and H_2O vapor and the lower molar volume of the solid product. During sulfidation, the "skin" remains relatively intact. Figures 3.17 and 3.18 show SEM micrographs of Z2T (calcined 720 C) after *ca.* 10% reduction and after 25% sulfidation, respectively. The beginning of fragmentation of the "skin" is evident in Figure 3.17. The following equations are obtained (Szekely et al., 1976) for the reaction $A(g) + bB(s) \rightarrow cC(g) + dD(s)$ assuming the reaction is only chemically

Figure 3.15 Comparison of experimental conversion profiles of ZnO reduced in 10%H₂-90%N₂ with profiles predicted from the grain model.

Figure 3.16 Comparison of experimental conversion profiles of Z2T reduced in 10%H₂-90%N₂ with profiles predicted from the grain model.

a)

b)

Figure 3.17 SEM micrographs of Z2T calcined at 720°C a) partially reduced (~10%) at 650°C in 10% H₂-90% N₂ b) magnification.

Figure 3.18 SEM micrograph of Z2T (calcined at 720°C) partially sulfided (~25%) at 650°C in 2% H₂S-1 H₂%-98% N₂.

controlled:

$$t^* = 1 - (1 - X)^{1/3} \quad (3.26)$$

$$t^* = (b/\rho_s R_o) R_o t \quad (3.27)$$

$$r_o = \frac{3}{A_o \rho_s} \quad (3.28)$$

where t^* is the dimensionless reaction time, ρ_s is the molar density of the solid B, r_o is the initial grain radius, R_o is the initial reaction rate, and A_o is the initial surface area of the solid B. As shown in Figures 3.15 and 3.16, the agreement between the predicted conversion profiles and the experimental profiles is good. For Z2T reduction, a product layer of TiO_2 is formed. Since the ratio of the solid product molar volume to the solid reactant molar volume is only 0.41, a porous product layer is formed. From the conversion profiles, this product layer poses no hindrance to reaction.

To determine the chemical phase transformations of the Zn-Ti-O solids during reduction, partially reacted solids were examined by XRD analyses. To obtain sufficient quantities of materials for analyses, 40-50 mg of solids were reacted in the TGA. Table 3.4 lists the results of the XRD analyses of various partially reduced solids. The reactions were performed at 650°C in 10 mol% H_2 -90 mol% N_2 . For Z2T, the following reactions appeared to occur during reduction:

Table 3.4 XRD analyses of reduced Zn-Ti-O solids.¹

Sample	Crystalline Phase (wt%)			
	Zn ₂ TiO ₄	Zn ₂ Ti ₃ O ₈	ZnTiO ₃	TiO ₂ (rutile)
Z2T, 31% reduced	76	24	0	0
Z2T, 74% reduced	0	85	0	15
Z2T, 100% reduced	0	0	0	100
Z3T, 53% reduced	75	25	0	0
Z2T3-b, 69% reduced	0	0	33	67

¹ reduced in the TGA at 650°C in 10 mol% H₂-90 mol% N₂

No corresponding change in the reaction rate accompanied the phase change from Zn_2TiO_4 to $\text{Zn}_2\text{Ti}_3\text{O}_8$. At conversions higher than 66%, the only reactive phase present was $\text{Zn}_2\text{Ti}_3\text{O}_8$. As shown in Figure 3.16, no noticeable change in the reduction rate was observed. For Z2T3-b, consisting of ZnTiO_3 and TiO_2 (Table 3.2), ZnTiO_3 reacted directly with H_2 to form $\text{Zn}(g)$ and $\text{TiO}_2(s)$. No intermediate chemical phases were detected. Although these XRD analyses revealed that the chemical phase transformations of Zn_2TiO_4 and ZnTiO_3 were different, these differences did not affect the initial reduction rate as discussed previously (Section 3.3.1).

After partial reduction of Zn-Ti-O solids, changes in the color of the solids were observed. ZnO which was initially white in color retained the same color after partial reduction. However, Zn-Ti-O solids which were also initially white took on a gray-blue color after partial reduction. Fully reduced Zn-Ti-O solids also had a gray color. This gray pigment was probably due to some surface reduction of TiO_2 . Ti_3O_5 has a blue-black color. No reduced TiO_2 phase was detected by XRD analyses which indicated that no bulk reduction of TiO_2 took place. In addition, the weight loss was not significantly different (within 5%) from what would be expected from the loss of only ZnO.

The solid structural changes in reduction were examined with a scanning electron microscope. Figure 3.19 shows the surfaces of ZnO unreacted and 31% reduced in 10 mol% H₂-90 mol% N₂ at 650°C. The solid which was calcined at 1000°C is very sintered. The unreacted solid is composed of overlapping grains with an average radius of 0.6-0.7 μm. Because of the overlapping grain structure, the predicted grain radius by Eq. 3.28 is greater (0.79 μm) than the observed radius. After 31% reduction, the grain radius is small (ca. 0.4-0.6 μm). This is consistent with a heterogeneous gas-solid reaction where the solid is composed of shrinking nonporous grains.

Figures 3.20 and 3.21 show the SEM micrographs of Z2T, calcined at 1000°C, unreacted and partially reduced (31%) at 650°C in 10 mol% H₂-90% N₂, respectively. As shown in Figure 3.20, Z2T is highly sintered. Overlapping grains with size in the range of 0.3-0.4 μm are present. After reaction (Figure 3.21), the size of the grains is smaller (ca. 0.2-0.3 μm). On the surface of these grains is a porous crystalline layer which is the TiO₂ product layer. The formation of a porous product layer where diffusion is rapid is consistent with the conversion profile. No decrease in reaction rate due to slow diffusion through the developing product layer was observed.

The reduction of Z9T which is composed of a mixture of ZnO and Zn₂TiO₄ is structurally interesting. Figure 3.22 shows the SEM micrographs of Z9T unreacted and partially reduced (45%) at 650°C in 10 mol% H₂-90 mol% N₂. The unreacted solid (Figure 3.22a) is composed of closely packed crystals (0.1-0.2 μm radius). After partial reduction (Figure 3.22b), it is apparent that some crystals were more reactive than others. Holes which are approximately hexagonal in shape were left where these crystals had reacted with

a)

b)

Figure 3.19 SEM micrographs of ZnO calcined at 1000°C a) unreacted and b) 31% reduced at 650°C in 10% H₂-90% N₂.

a)

b)

Figure 3.20 SEM micrographs of a) unreacted Z2T calcined at 1000°C and b) magnification of (a).

a)

b)
 Figure 3.21 SEM micrographs of a) ZrTi (calcined at 1000°C) after 31% reduction at 650°C in 10% H₂-90% N₂ and b) magnification of (a)

Figure 3.22 SEM micrographs of Z9T calcined at 1000°C a) unreacted and b) 45% reduced at 650°C in 10% H₂-90% N₂.

H₂. It is surmised that these were ZnO crystals. ZnO crystallizes in the close-packed hexagonal system. Also, ZnO is more reactive in reduction than Zn₂TiO₄. The cubic Zn₂TiO₄ crystals, however, react much slower than ZnO, and, as can be seen in Figure 3.22b, the sizes of the remaining crystals were relatively unchanged after 45% conversion.

3.4 SUMMARY/CONCLUSIONS

A detailed study of hydrogen reduction of bulk Zn-Ti-O materials has been undertaken in this work, aimed at determining whether Zn-Ti-O materials are intrinsically more resistive to reduction than ZnO, and if so, to identify the Zn-Ti-O composition(s) that suppress reduction rate the most.

In reaction with H₂-N₂ gas mixtures (0% H₂O), Zn-Ti-O solids had a lower reduction rate than ZnO at temperatures in the range of 550-1050°C. With solids containing (Zn/Ti)_{atomic} ≤ 3, the initial reduction rate was ten times slower than that of ZnO at 700°C. The activation energy of reduction was 37 and 24 kcal/mol, respectively, for Zn-Ti-O and ZnO.

All zinc titanate phases (i.e. Zn₂TiO₄, Zn₂Ti₃O₈ and ZnTiO₃) had the same initial rate of reduction. Increasing the amount of TiO₂ beyond 25 mol% (75 mol% ZnO) did not correspondingly decrease the reduction rate in the absence of water vapor.

Water vapor inhibited the initial reduction rate of ZnO and Zn-Ti-O solids. However, increasing the water vapor content from 1 to 8 mol% did not cause any further decrease in the reduction rate. Addition of water vapor was accompanied by changes in the activation energies to 44 kcal/mol for both ZnO and Zn-Ti-O solids. Increasing the relative amount of TiO₂ from 0 mol% to 60 mol% was accompanied by a corresponding decrease

in the reduction rate.

From the reduction of partially sulfided ZnO and Zn-Ti-O solids, it appeared that H₂S inhibited the initial reduction rate similar to H₂O.

Two reduction sites are proposed for ZnO reduction. Type A sites which are very reactive but can be poisoned by H₂O and type B sites which are less reactive.

Titanium addition reduces the number of type A sites. Approximately 25 mol% TiO₂ (with 75 mol% ZnO) will completely eliminate type A sites. With $(\text{Zn/Ti})_{\text{atomic}} \leq 3$, another type of reaction sites, type A', less reactive than type A sites, is involved in reduction. However, in the presence of H₂O or H₂S, these sites are eliminated and type B sites dominate reduction. Type B sites are less sensitive to titanium than type A sites, thus requiring higher relative amounts of TiO₂ to deactivate.

The geometric interaction of titanium with type A and B sites of zinc oxide is believed to cause elimination of these sites. Whether this property is unique to titanium is not clear at the present time. In the early work of Hirschwald and Noack (1972) the reduction suppression imparted on ZnO by lithium, aluminum and gallium oxides was attributed to an electronic effect. On the other hand, as mentioned in the "Introduction", the addition of iron oxide in ZnO in the form of the compound zinc ferrite, ZnFe₂O₄, provides no stability to ZnO against reduction. This may be due to the fact that ZnFe₂O₄ breaks up into ZnO and Fe₃O₄ (or lower valence iron oxides) in a reducing gas atmosphere. In the present study no free ZnO was found in the zinc titanate compounds reacted in hydrogen. Perhaps the ability of titanium to remain intimately associated with ZnO and, thus, possibly the reactive sites, in a reducing atmosphere can explain why Zn-Ti-O solids

have lower reduction rates than Zn-Fe-O solids. Clearly, however, more information on the effect of various oxides on the reduction stability of ZnO is needed to elucidate the interaction mechanism.

4. SULFIDATION OF ZN-TI-O MATERIALS

4.1 BACKGROUND

A main objective of this project was to evaluate the Zn-Ti-O sorbents for high temperature gas desulfurization. Zinc titanate promoted with hydrodesulfurization catalysts has been reported (Farha, Jr. and Gardner, 1982) to convert organic sulfur liquids to H_2S and to remove H_2S by absorption over the temperature range of 205-583°C. The sulfided material was more easily regenerated in air than bulk ZnS. Zinc sulfate was not formed during regeneration at 650°C. From the free energy data given in Barin and Knacke (1973) and Barin et al. (1976), the zinc orthotitanate phase, Zn_2TiO_4 , has slightly lower H_2S removal efficiency than ZnO (Fig. 3.1). No thermodynamic data were found for the other possible zinc titanate phases (i.e. $ZnTiO_3$ and $Zn_2Ti_3O_8$). In previous work in this laboratory cyclic sulfidation-regeneration tests with various compositions of Zn-Ti-O sorbents were carried out in bench-scale, packed-bed reactors (Flytzani-Stephanopoulos et al., 1987; Lew, 1987; Lew et al., 1989). Hydrogen sulfide removal efficiencies were found to be comparable to those of ZnO. Also, inclusion of CO and CO_2 in the synthetic gas mixture used for sulfidation did not affect the sorbent performance. In other work, zinc titanates prepared and tested in pellet form were found to have high crush strength and to retain their strength

after sulfidation (Flytzani-Stephanopoulos, et al., 1988; Gangwal, 1989).

The objectives of the sulfidation research conducted in this project were to (1) measure the sulfidation kinetics of various compositions of bulk Zn-Ti-O sorbents and compare them to results obtained for ZnO, (2) examine the structural and chemical changes of sorbents during sulfidation, (3) determine the effect of hydrogen and water vapor in the reactant gas stream, and (4) identify the range of Zn-Ti-O compositions that has the most desirable overall sulfidation performance.

4.2 EXPERIMENTAL METHODS

Sulfidation experiments with sorbents containing various Zn/Ti ratios were performed. The preparation and characterization of the sorbents were discussed in Section 2. The reacted sorbents were characterized by various physical and chemical techniques which were also discussed in Section 2. These analytical techniques include BET-N₂ desorption for surface area measurement, mercury porosimetry for pore volume measurement, scanning electron microscopy (SEM) coupled with energy dispersive X-ray (EDS) analysis for surface morphology and elemental distribution determination, and X-ray diffraction for crystalline phase identification. The chemical and physical properties of the sorbents used in sulfidation are shown in Tables 4.1 and 4.2, respectively.

Kinetic experiments were performed in the TGA system described in Section 3. The TGA measured the weight increase as a function of the time associated with hydrogen sulfide uptake. The reactant gas was introduced into the apparatus through a side arm (Figure 4.1). The balance section of the TGA was continuously purged with a protective nitrogen gas flow (*ca.* 200 cm³/min) which also served as a diluent for the reactant stream.

Table 4.1 Chemical Properties of Sorbents Used in Sulfidation Experiments ¹

Sorbent	(Zn/Ti) (atomic ratio)	Crystalline Phases (wt %)				
		ZnO	Zn ₂ TiO ₄	ZnTiO ₃	Zn ₂ Ti ₃ O ₈	TiO ₂
Z3T7 ²	3/7	0	0	69	0	31
Z2T3-a	2/3	0	0	65	16	19
Z2T3-b	2/3	0	0	83	0	17
ZT	1/1	0	20	45	35	0
Z3T2	3/2	0	68	18	14	0
Z2T-a	2/1	0	100	0	0	0
Z2T-b ³	2/1	0	100	0	0	0
Z3T	3/1	28	72	0	0	0
ZnO	---	100	0	0	0	0

¹ Prepared from zinc acetate and titanium (IV) i-propoxide with 1:1 mole ratio of metal ions to citric acid (unless otherwise noted). Calcined at 720°C for 12 h.

² Prepared with titanium tetrachloride.

³ Prepared with 1:2 mole ratio of metal ions to citric acid.

Table 4.2 Physical Properties of Sorbents Used in Sulfidation Experiments ¹

Sorbent	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Pore Size Distribution ² (%), μm (diameter)
Z3T7 ³	5.4	1.26	16.0%, > 25 μm 69.5%, 25-1 μm 13.3%, 1-0.1 μm 1.2%, 0.1-0.003 μm
Z2T3-a	2.3	0.47	58.5%, >25 μm 21.8%, 25-1 μm 10.8%, 1-0.1 μm 8.9%, 0.1-0.003μm
Z2T3-b	1.3	0.29	44.8%, >25 μm 25.4%, 25-1 μm 12.6%, 1-0.1 μm 17.2%, 0.1-0.003μm
ZT	1.6	0.57	15.7%, >25 μm 67.2%, 25-1 μm 7.9%, 1-0.1 μm 9.2%, 0.1-0.003μm
Z3T2	2.2	0.72	44.2%, >25 μm 38.4%, 25-1 μm 10.5%, 1-0.1 μm 6.9%, 0.1-0.003μm

Table 4.2 Physical Properties of Sorbents Used in Sulfidation Experiments ¹ (cont'd)

Sorbent	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Pore Size Distribution ² (%), μ m (diameter)
Z2T-a	4.1	0.73	56.2%, >25 μ m 28.1%, 25-1 μ m 5.8%, 1-0.1 μ m 9.9%, 0.1-0.003 μ m
Z2T-b ⁴	13.9	1.13	10.0%, >25 μ m 53.4%, 25-1 μ m 15.3%, 1-0.1 μ m 21.3%, 0.1-0.003 μ m
Z3T	7.6	0.93	19.6%, >25 μ m 54.6%, 25-1 μ m 10.0%, 1-0.1 μ m 15.8%, 0.1-0.003 μ m
ZnO	2.4	1.20	15.0%, >25 μ m 62.2%, 25-1 μ m 21.1%, 1-0.1 μ m 1.7%, 0.1-0.003 μ m

¹ Prepared from zinc acetate and titanium (IV) i-propoxide with 1:1 mole ratio of metal ions to citric acid. Calcined at 720°C for 12 h. (unless otherwise noted)

² Pore size distribution for 90-125 μ m particles except for Z2T3-b with 420-840 μ m particles.

³ Prepared with titanium tetrachloride.

⁴ Prepared with 1:2 mole ratio of metal ions to citric acid.

Figure 4.1 Schematic of TGA reactor system.

Gas flow rates were set by Brooks Model 5850E mass flow controllers. To accommodate corrosive gases such as hydrogen sulfide, the sample was placed on a quartz pan suspended by a quartz hangdown wire. Previously, a Nichrome hangdown wire was used. However, H_2S was observed to corrode the wire. Platinum pans were not used because it is known that platinum catalyzes the H_2S decomposition (Fukuda et al., 1978; Bartholomew et al., 1982; Patrick, 1988). In regards to gas diffusion problems, it was experimentally verified that a gas flow rate of typically between 300-400 sccm with a sample size between 1-3 mg minimized external mass transfer effects. Particle sizes needed to minimize pore diffusional effects were typically between 88-125 μm (120-170 mesh).

For sulfidation, a reactant gas mixture containing $\text{H}_2\text{S-H}_2\text{-N}_2$ was used. In several experiments, H_2O vapor was added. Various compositions were used to determine the effects of H_2 and H_2O on sulfidation. Water vapor was added to the gas by bubbling nitrogen and hydrogen through a water saturator maintained at room temperature (25°C) in a three-neck flask assembly. The saturated gas stream was then mixed with the $\text{H}_2\text{S-N}_2$ gas stream and entered the reactor through the side arm.

4.3 PRESENTATION AND DISCUSSION OF SULFIDATION RESULTS

4.3.1 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 sorbents containing various atomic ratios of Zn:Ti and various chemical phases (e.g. ZnO , Zn_2TiO_4 , ZnTiO_3 , and $\text{Zn}_2\text{Ti}_3\text{O}_8$). Kinetic parameters (e.g. activation energies) were determined from these experiments. The possible overall reactions in sulfidation are:

Table 4.3 lists the K_{eq} for these reactions. No thermodynamic data were found for either ZnTiO_3 or $\text{Zn}_2\text{Ti}_3\text{O}_8$. Two types of ZnS may form. One is β -ZnS (sphalerite) which exists in a cubic crystalline form. The other is α -ZnS (wurtzite) which exists in a hexagonal crystalline form. At temperatures above 1020°C, β -ZnS is transformed to α -ZnS. Formation of β -Zns is slightly more thermodynamically favorable yielding higher K_{eq} . The reaction of titanium dioxide with hydrogen sulfide (reaction 4.5) is thermodynamically unfavorable. At 1000 K, the K_{eq} for reaction (4.5) is 5.67×10^{-9} for anatase and 1.53×10^{-9} for rutile. Anatase is a metastable high surface area structure which upon heating above 750°C, transforms into the denser rutile structure. This transformation is associated with a significant surface area loss. To check whether there was any absorption of H_2S on TiO_2 , 2 mol% H_2S -1 mol% H_2 -97 mol% N_2 was passed over TiO_2 at 700°C. Figure 4.2 shows the results of experiments with both the anatase (from Aldrich Chemical Co.) and rutile (UCI 1090-113 extrusions crushed to 90-125 μm size particles) forms of titanium dioxide. Negligible weight change was measured for either type of TiO_2 .

Figure 4.2 Reaction of TiO_2 with H_2S at 700°C .

Figure 4.3 Effect of gas flowrate on the initial reaction rate of ZnO at 700°C .

Table 4.3 Equilibrium Constants and Heats of Reaction for Sulfidation Reactions at 727°C

<u>Reaction</u>	<u>Thermodynamic Constants</u>	
	K_{eq}	ΔH , kcal/mol
$ZnO + H_2S = \beta\text{-}ZnS + H_2O$	7.21×10^4	-18.97
$ZnO + H_2S = \alpha\text{-}ZnS + H_2O$	1.03×10^4	-15.81
$1/2Zn_2TiO_4 + H_2S = \beta\text{-}ZnS + 1/2TiO_2 + H_2O$	4.61×10^3	-18.98
$1/2Zn_2TiO_4 + H_2S = \alpha\text{-}ZnS + 1/2TiO_2 + H_2O$	3.22×10^3	-15.82
$1/2TiO_2(\text{anatase}) + H_2S = 1/2TiS_2 + H_2O$	5.67×10^{-9}	18.76
$1/2TiO_2(\text{rutile}) + H_2S = 1/2TiS_2 + H_2O$	1.53×10^{-9}	20.35

Reactions 4.1 and 4.2 are exothermic. In Table 4.3, the heats of reaction at 1000 K are also listed. Since these reactions are exothermic, it is necessary to investigate the possible temperature excursion which may occur during the reaction. Calculations were based on reaction with a gas containing 2 mol% H₂S-1 mol% H₂-97 mol% N₂ at 1000 K. Because the gas contains mainly N₂, the properties of the reactant gas (i.e. viscosity, density, and heat capacity) were assumed to be the same as those for pure N₂. The inside diameter of the reactor is 1.6 cm, and the particle diameter is 1.25x10⁻² cm. To calculate the Reynolds number, a typical gas flowrate of 350 sccm was used. The maximum possible temperature increase for reactions (4.1) and (4.2) assuming β -ZnS as a product is less than 1°C. For α -ZnS formation, the temperature change is smaller. It was, therefore, concluded that the isothermal assumption was valid.

The reactant gas used in the sulfidation kinetics experiments contains 2 mol% H₂S-1 mol% H₂-97 mol% N₂. Hydrogen was added to the gas to inhibit the decomposition of H₂S. The decomposition reaction is:

At 1000 K and a gas flowrate of 350cm³/min, the equilibrium decomposition rate due to reaction (4.6) is 93 mg S₂/h in the absence of hydrogen. The sulfur will deposit on the cooler section of the reactor downstream of the sample pan. With 1 mol% H₂ in the gas stream, the rate decreases to 11 mg S₂/h. This decomposition rate is low compared to the total H₂S in the reactant gas (549 mg S₂/h). The presence of 10 mol% H₂ will decrease the rate of decomposition even further (0.1 mg S₂/h). However, as will be discussed in Section 4.3.4, no significant difference in the sulfidation profiles was observed in the presence of

different concentrations of hydrogen at temperatures up to and including 700°C. This indicates that the effect of gaseous S_2 is negligible.

To ensure that these results were obtained in the absence of diffusional limitations, either external (i.e. gas-film diffusion) or internal (i.e. intra-particle diffusion), the gas flow rate, the sample size, and the particle size were varied. In preliminary experiments, the effect of gas flow rate on the reaction rates was examined. Approximately 1-3 mg of sample were used. The results for ZnO sulfidation are depicted in Figure 4.3, which shows that above approximately 300 sccm the gas flow rate has no effect on the initial reaction rate of 700°C. Similar results were obtained for the sulfidation of the other sorbents. This indicates that above 300 sccm external mass transfer effects were eliminated. All sulfidation experiments were subsequently conducted with a gas flow rate of 350 sccm.

Different particle sizes were examined to minimize the effect of internal mass transfer. In Figure 4.4, the result for this set of sulfidation experiments is shown for two ranges of particle sizes, 420-480 μm and 90-125 μm , with sorbents ZnO, Z2T-a, and Z2T3-a. These experiments were performed at 700°C. The results are shown in terms of fractional conversion (X) versus reaction time (minutes). The fractional conversion is based on conversion to ZnS. The data from these experiments appear to show little effect on the rate of reaction for all sorbents except Z2T-a. However, when even smaller particle sizes (43-63 μm) were used for Z2T-a as shown in Figure 4.5, although no change in the initial sulfidation rate occurred, a significant effect was seen at higher fractional conversion. No difference in the sulfidation profile was observed with 43-63 μm particles for Z2T3-a. It was, therefore, decided to use 90-125 μm size particles for all sorbents except Z2T-a, for

Figure 4.4 Effect of particle sizes, 420-840 and 90-125 μm , for sorbents ZnO, Z2T-a and Z2T3-a on sulfidation conversion profiles.

Figure 4.5 Effect of particle sizes, 90-125 and 43-63 μm , for sorbents Z2T-a and Z2T3-a on sulfidation conversion profiles.

which 43-63 μm size particles were used.

Initial rate measurements were performed with the sorbents listed in Tables 4.1 and 4.2. The results of these experiments at 600 and 700°C in 2 mol% H_2S -1 mol% H_2 -97 mol% N_2 are shown in Figure 4.6. The initial rate is expressed in mmol ZnS formed/ $\text{cm}^2\cdot\text{s}$. The rate was normalized with the initial surface area of the sorbent. The initial rate of sulfidation for ZnO at 700°C is approximately 1.2-1.8 times higher than for all Zn-Ti-O sorbents containing ≥ 25 mol% Ti (based on Zn-Ti stoichiometry). At 600°C, the ZnO sulfidation rate is approximately 1.5 times higher than that of Zn-Ti-O sorbents.

A significant finding of this work is that the initial sulfidation rate was similar for different zinc titanate phases. Sorbents with different Zn-Ti compositions will form different zinc titanate phases as shown in Table 4.2. A sorbent with 30 mol% ZnO-70 mol% TiO_2 forms a mixture of ZnTiO_3 and TiO_2 , while a sorbent with 75 mol% ZnO-25 mol% TiO_2 forms a mixture of Zn_2TiO_4 and ZnO. However, both of these sorbents had approximately the same initial sulfidation rates (Figure 4.6).

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 Z2T-a, a sorbent prepared with 2:1 atomic ratio of Zn:Ti, and Z2T3-a which was prepared with 2:3 atomic ratio of Zn:Ti. Zn_2TiO_4 was the only crystalline phase determined by XRD in Z2T-a, while Z2T3-a contained a mixture of ZnTiO_3 , $\text{Zn}_2\text{Ti}_3\text{O}_8$ and TiO_2 . As shown in the X-ray diffractogram of Z2T-a (Figure 4.7), the peaks are very narrow which is consistent with a highly crystalline material. For the purpose of comparison and in order

Figure 4.6 Initial sulfidation rate of several Zn-Ti-O sorbents in 2% H₂S-1% H₂-97% N₂ at 600 and 700°C.

Figure 4.7 X-ray diffractogram of sorbent Z2T-a (2 Zn : 1 Ti) calcined at 720°C.

to establish a baseline sulfidation performance level to meet or perhaps exceed, similar kinetic experiments were also performed with ZnO.

In the absence of both diffusional and mass transfer resistances, an intrinsic initial heterogeneous rate expression of the form

$$R_0 = k C_{H_2S}^n \quad (4.7)$$

was used, 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 [cm/s], C_{H_2S} is the molar concentration of hydrogen sulfide [mmol/cm³], and n is the reaction order. An Arrhenius relationship can be used to express the intrinsic rate constant as

$$k = k_0 \exp[-E/RT] \quad (4.8)$$

In equation (4.8) k_0 is the Arrhenius frequency factor, E is the activation energy, R is the ideal gas constant, and T is the absolute temperature.

The reaction orders (n) for ZnO and Z2T-a sulfidation were both determined to be one. Figure 4.8 illustrates the results obtained for ZnO and Z2T-a sulfidation. The linearity of the variation in initial sulfidation rate with changing hydrogen sulfide concentration indicates a reaction order of one. This agrees with the data reported by Westmoreland et al. (1977) for zinc oxide.

The Arrhenius dependence of ZnO-H₂S and Z2T-H₂S reactions was determined by measuring the initial sulfidation rate as a function of temperature. The experiments were performed in 2 mol% H₂S-1 mol% H₂-97 mol% N₂. Figure 4.9 shows the resultant Arrhenius plots for ZnO and Z2T-a sulfidations. The intrinsic sulfidation rate for ZnO is

Figure 4.8 Determination of reaction order for a) ZnO-H₂S and b) Z2T-H₂S reactions.

Figure 4.9 Comparative Arrhenius plots for ZnO-H₂S and Z2T-H₂S reactions.

Figure 4.10 Comparative Arrhenius plots for Z2T3-H₂S and Z2T-H₂S reactions.

greater than Z2T-a at all temperatures between 400-700°C. Kinetic constants obtained for the ZnO-H₂S and Z2T-H₂S systems are listed in Table 4.4. The activation energies for both ZnO and Z2T-a sulfidation are approximately the same (10.3 kcal/mol and 9.3 kcal/mol, respectively). The major difference is in the frequency factors. The frequency factor for ZnO sulfidation is approximately three times greater than that for Z2T-a. The lower frequency factor for the latter is probably caused by fewer reaction sites on the surface of the reactant solid due to the presence of titanium. Thus, the lower values of the initial rate are somewhat deceptive because the surface area used in the calculation of the frequency factor is the total surface area (ZnO+TiO₂) and not the specific surface area (ZnO only). Also, another possible reason for the lower initial rate may be the interaction of titanium with a reactive site to decrease its reactivity. What is important to note is that sorbents prepared with higher amount of TiO₂ do not have correspondingly lower initial reaction rates as shown in Figure 4.6. Thus, as the concentration of TiO₂ in the sorbent increases, there is not a corresponding decrease in the number of reactive sites. As shown in Figure 4.10, sorbent Z2T3-a has a nearly identical Arrhenius plot to sorbent Z2T-a.

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" diam. and L/D=2.5) under conditions not free from mass transfer and pore diffusion limitations. Clearly such "kinetic" measurements with pellets provide apparent reaction rates, are pellet-specific and cannot be used to obtain values for intrinsic kinetic parameters, such as the activation energy.

Table 4.4 Arrhenius Constants for Sulfidation Reactions

<u>Reaction</u>	<u>Temp. Range °C</u>	<u>Arrhenius Constants</u>	
		k_0 , cm/s	E, kcal/mol
$\text{ZnO} + \text{H}_2\text{S} \rightarrow \text{ZnS} + \text{H}_2\text{O}$	400-700	1.31	10.3
$\text{ZnO} + \text{H}_2\text{S} \rightarrow \text{ZnS} + \text{H}_2\text{O}$ (Westmoreland et al., 1977)	300-750	0.11	7.2
$1/2\text{Zn}_2\text{TiO}_4 + \text{H}_2\text{S} \rightarrow$ $\text{ZnS} + 1/2\text{TiO}_2 + \text{H}_2\text{O}$	400-700	0.40	9.3

Table 4.5 Specific Surface Areas of ZnO Samples

<u>Source</u>	<u>Surface Area, m²/g</u>
amorphous citrate technique, calcined at 720°C, 12h	2.4
EM Science	3.7
Matheson Coleman & Bell (Westmoreland et al., 1977)	4.9

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), see Table 4.4. Because the Matheson Coleman & Bell zinc oxide used by these authors was no longer available, zinc oxide was purchased from EM Science which took over most of Matheson Coleman & Bell production. In Table 4.5, the specific surface areas of these zinc oxide samples are listed. As shown in Figure 4.11, the Arrhenius plot for sulfidation of the (EM Science) ZnO sample was in much better agreement with that of Westmoreland et al. (1977) than the ZnO prepared from the amorphous citrate technique. 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. Variation in exposed crystal faces can cause differences in reactivity in structure-sensitive reaction systems. To determine whether any difference in crystal geometry and, thus, perhaps, crystal orientation was present, the surfaces of ZnO prepared by the amorphous citrate technique and the ZnO obtained from EM Science were examined with the scanning electron microscope. The SEM micrographs for both ZnO types are shown in Figure 4.12. Clearly, different crystal geometries were 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.

4.3.2 Conversion Profiles of Bulk Zn-Ti-O Sorbents

The sulfidation reactions of three sorbents, ZnO, Z2T-a, Z2T3-a were studied in detail. Figure 4.13 shows the conversion profiles for these sorbents at 650°C. Conversion was defined as follows

Figure 4.11 Comparative Arrhenius plots for several ZnO samples.

a) 5000x

b) 10000x

Figure 4.12 SEM micrographs of ZnO (EM Science) a) 5000x and b) 10000x.

c) 5000x

d) 10000x

Figure 4.12
(cont'd.)

SEM micrographs of ZnO (amorphous citrate technique, calcined at 720°C)
a) 5000x and b) 10000x.

Figure 4.13 Comparative conversion profiles for sorbents ZnO, Z2T-a and Z2T3-a.

Figure 4.14 Comparative plots of reaction rates for sorbents ZnO, Z2T-a and Z2T3-a.

$$X = (W_i - W)/(W_i - W_f^I) \quad (4.9)$$

where W is the weight, W_i is the initial weight and W_f^I 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).

To gain complementary information, the data for Figure 4.13 are plotted in the form of the reaction rate as a function of conversion in Figure 4.14. The reaction rate decreases with conversion. The decreasing reaction rate is due both to formation of the product layer ($\text{ZnS} + \text{TiO}_2$) as well as to a decrease in the reaction surface area. The latter statement is generally true if the sorbents are not comprised of plate-shaped grains. In the case of ideal plate-shaped grains of infinite length, no change in the reaction surface area will occur until the sorbent is completely reacted. For Z2T3-a, the drop in the reaction rate is much more pronounced than for ZnO . As will be discussed in Section 5, this is due to non-uniform grain size distribution and slower diffusion through the product layer of ZnS and TiO_2 than for just ZnS alone.

In Section 4.3.1, it was shown that the initial sulfidation rates of sorbents composed of $(\text{Zn}/\text{Ti})_{\text{atomic}} \leq 3/1$ were approximately the same. To determine whether this rate similarity is due to reaction of similar intermediate phases, XRD analyses were performed on partially sulfided samples. The samples were sulfided in the TGA at 650°C in 2 mol% H_2S -1 mol% H_2 -97 mol% N_2 . To provide sufficient amount of samples for analysis, 20-30 mg were used. This is a much larger quantity than what was used for kinetic experiments (1-3 mg). The results of these analyses are shown in Table 4.6. Because Z2T3-a contained

Table 4.6 XRD Analyses of Sulfided Sorbents ¹

Sample	Crystalline Phases (wt %)						
	ZnO	Zn ₂ TiO ₄	Zn ₂ Ti ₃ O ₈	ZnTiO ₃	α-ZnS	β-ZnS	TiO ₂ (anatase)
Z2T -a	0	100	0	0	0	0	0
48% sulfided	0	23	35	0	16	26	negligible
95% sulfided	0	0	6	0	17	53	24
Z2T3-b							
35% sulfided	0	0	0	48	15	0	37
ZnO							
100% sulfided	0	0	0	0	33	67	0

¹ Sulfided at 650°C in 2% H₂S-1% H₂-97% N₂.

two zinc titanate phases (i.e. ZnTiO_3 and $\text{Zn}_2\text{Ti}_3\text{O}_8$), it was difficult to analyze the phase changes. After partial sulfidation, its XRD-analysis showed ZnTiO_3 , $\text{Zn}_2\text{Ti}_3\text{O}_8$, ZnS , and TiO_2 . It was, thus, unclear whether additional $\text{Zn}_2\text{Ti}_3\text{O}_8$ was being formed during sulfidation. To overcome this difficulty, another sorbent with $(\text{Zn}/\text{Ti})_{\text{atomic}} = 2/3$, designated Z2T3-b was prepared with a composition of 83 wt% ZnTiO_3 and 17 wt% TiO_2 (Table 4.1). From the XRD analysis of partially sulfided Z2T3-b, it was determined that ZnTiO_3 reacted directly with H_2S to form $\alpha\text{-ZnS}$ and TiO_2 (rutile) by:

No intermediate zinc titanate phases were detected.

The sulfidation of Z2T-a was more complex. During sulfidation, the phases $\text{Zn}_2\text{Ti}_3\text{O}_8$, $\alpha\text{-ZnS}$ and $\beta\text{-ZnS}$ were formed. Zn_2TiO_4 exists as a cubic spinel, while $\text{Zn}_2\text{Ti}_3\text{O}_8$ has a defect spinel structure. It is proposed that the abstraction of Zn from Zn_2TiO_4 to form ZnS produces the defect spinel phase. The reactions which occur for Zn_2TiO_4 are then the following:

No significant amount of free TiO_2 was detected for the Z2T-a sample sulfided to 48%. This indicates that $\text{Zn}_2\text{Ti}_3\text{O}_8$ reacted much slower than Zn_2TiO_4 . If this was true, a noticeable drop in the reaction rate would be observed at 66% conversion (complete conversion to $\text{Zn}_2\text{Ti}_3\text{O}_8$ and ZnS based on stoichiometry). To determine the validity of this argument, experiments were performed with a different sample, Z2T-b. Z2T-b consists of

100% Zn_2TiO_4 , similarly to Z2T-a. However, Z2T-b was prepared with a more uniform grain structure (by doubling the citric acid/metal ratio in the precursor solution). Figure 4.15 shows the difference in grain structure of Z2T-a and Z2T-b. Z2T-a has very non-uniform grain size distribution. Both small grains (radius, $r=0.05\ \mu\text{m}$) and much larger grains ($r = 0.1\text{-}0.2\ \mu\text{m}$) are present. The size of the large grains in Z2T-a was difficult to estimate from the SEM micrographs (Figure 4.15). They appear to be large plates whose thickness is hard to estimate. Z2T-b, on the other hand, has more uniform grains of approximately $0.02\ \mu\text{m}$ radius. Also on Z2T-a, the formation of a "skin" of relatively low porosity was observed (discussed in Section 2). Crushing the sorbent to smaller particle sizes exposed the more porous interior. This "skin" had lower reactivity than the interior. Figure 4.16 shows an SEM micrograph of Z2T-a $\sim 90\%$ sulfided with 2 mol% H_2S -1 mol% H_2 -97 mol% N_2 at 650°C . Part of the surface "skin" had been removed (perhaps, by crushing the sorbent) prior to sulfidation. EDS analyses of the $\sim 90\%$ sulfided sorbent of Figure 4.16 found that the exposed interior was more sulfided ($\text{S}/\text{Zn}=1.0$, $\text{Zn}/\text{Ti}=2.3$) than the "skin" ($\text{S}/\text{Zn}=0.7$, $\text{Zn}/\text{Ti}=2.4$). Thus, a combination of the "skin" effect and variation in particle sizes can explain changes in the reaction rate of Z2T-a. Z2T-b was chosen because it was easier to determine whether changes in the reaction rate were due to changes in its chemical phases rather than its physical structure. As shown in the conversion profile for Z2T-b in Figure 4.17, the slope of the curve remained constant up to approximately 90% conversion. Thus, $\text{Zn}_2\text{Ti}_3\text{O}_8$ has approximately the same sulfidation rate as Zn_2TiO_4 . This agrees with the initial rate measurements performed with sorbents containing different chemical phases. Sorbent ZT which contained 55 wt% $\text{Zn}_2\text{Ti}_3\text{O}_8$ and 45 wt% ZnTiO_3 did not have

Figure 4.15 SEM micrographs of unreacted (calcined at 720°C) a) Z2T-a and b) Z2T-b.

Figure 4.16 SEM micrograph of 90% sulfided Z2T-a at 650°C in 2% H₂S-1% H₂-97% N₂. (Interior: S/Zn=1.0 and "Skin": S/Zn=0.7)

Figure 4.17 Sulfidation conversion profiles for Z2T-a and Z2T-b.

Figure 4.18 Surface area change (based on initial surface area) of sorbents after 90% sulfidation.

significantly different initial sulfidation rate than sorbent Z2T-b (100 wt% Zn_2TiO_4). The reason that no significant amount of free TiO_2 was detected in the partially reacted Z2T-a sorbent must then be attributed to a rapid reaction of any TiO_2 formed with Zn_2TiO_4 to produce $\text{Zn}_2\text{Ti}_3\text{O}_8$

4.3.3 Physical Changes of Sorbents During Sulfidation

This section discusses the structural effects of sulfidation. Surface area changes along with morphological changes were examined. The samples were sulfided in the TGA at 650°C with 2 mol% H_2S -1 mol% H_2 -97 mol% N_2 . Again, to obtain sufficient quantity of samples for accurate measurements of the surface area, a large amount (40-60 mg) of sample was used. The samples were sulfided to approximately 90% conversion, and the surface areas were measured. Figure 4.18 shows the changes in surface area due to sulfidation. Lower surface area (29% lower than the initial area) was measured for ZnO after sulfidation. This can be attributed to a combination of sintering and grain overlapping in the product layer. If no sintering occurred and the sorbent was composed of non-interacting isolated grains (i.e. with non-overlapping product layers of different grains), the surface area should increase by 16%. However, if overlapping of the product layer is allowed, this would contribute to the observed surface area decrease. The Tamman temperature of ZnO is 849°C while that of $\alpha\text{-ZnS}$ is 713°C. Thus, $\alpha\text{-ZnS}$ sinters at a lower temperature than ZnO .

The surface area of Zn-Ti-O sorbents after sulfidation did not decrease as much as

for ZnO. As the amount of TiO_2 increases from 0 mol% to 60 mol%, sintering decreases concomitantly. Z2T3 (60 mol% TiO_2) after 90% sulfidation had a surface area 20% higher than in fresh form. However, Figure 4.18 is somewhat deceptive. When sulfidation of higher surface area-materials was performed, the percentage loss in surface area after sulfidation (ca. 90% sulfided, 90 min) was approximately the same as that of ZnO. For example, Z2T-b with an initial surface area value of $13.9 \text{ m}^2/\text{g}$ lost 40% of it after sulfidation at 650°C ($8.4 \text{ m}^2/\text{g}$). Correspondingly, a higher surface area ZnO ($5.2 \text{ m}^2/\text{g}$) had a 38% drop in its surface area after sulfidation ($3.2 \text{ m}^2/\text{g}$). Similarly, sorbent Z3T with an initial surface area of $7.6 \text{ m}^2/\text{g}$ decreased by 44% to $4.2 \text{ m}^2/\text{g}$ after sulfidation. Thus, the sintering rate was approximately the same for all materials. Pre-sintered sorbents were then examined in sulfidation. As can be seen in Figure 4.19, the equilibrium surface area of the sulfided sorbents is higher for higher TiO_2 -content. The initial values of the surface area of the sorbents shown in Figure 4.19 are listed in Table 4.7. Finally the (greater than ZnO) increase in surface area of Zn-Ti-O sorbents after sulfidation is not due to the formation of free TiO_2 with a higher surface area. When TiO_2 was calcined at the same temperature and for the same length of time as ZnO, the surface area of ZnO was 1.3 times higher than that of TiO_2 .

Although sulfidation of several sorbents, such as Z3T, was accompanied by a loss in surface area, after regeneration the surface area recovered and exceeded its original value. Using sorbent Z3T, sulfidation was performed in 2 mol% H_2S -1 mol% H_2 -97 mol% N_2 at 650°C . Air was used to regenerate the sorbent, also at 650°C . Three cycles of sulfidation-regeneration were performed. As shown in Figure 4.20, after the first cycle, the surface area

Figure 4.19 Surface area of sorbents before and after sulfidation.

Figure 4.20 Surface area of sorbent Z3T after successive sulfidation/regeneration cycles.

Table 4.7 Initial surface areas of the sorbents shown in Figure 4.19¹

<u>Zn/Ti</u>	<u>mol% TiO₂</u>	<u>Surface Area (m²/g)</u>
ZnO	0	0.68
3/1	25	0.68
2/1	33	0.76
1/1	50	0.40
2/3 (Z2T3-b)	60	1.30

¹ Surface area was reduced by heating all solids (calcined at 720°C, 12 h) except for Z2T3-b at 1000°C for 1 h. Z2T3-b was used without further heat treatment.

of Z3T increased from $7.6 \text{ m}^2/\text{g}$ to $12.0 \text{ m}^2/\text{g}$. After the succeeding cycles, the surface area decreased slightly. In comparison, the increase in the surface area of ZnO (initial surface area $2.4 \text{ m}^2/\text{g}$) was greater ($13.1 \text{ m}^2/\text{g}$) after regeneration in one cycle. Surface "roughening" of regenerated ZnO has been reported in earlier work in this laboratory (Flytzani-Stephanopoulos et al., 1987).

Scanning electron micrographs of unreacted ($2.4 \text{ m}^2/\text{g}$) and sulfided ZnO are shown in Figure 4.21. The assumption of isolated grains is incorrect, as can be seen in Figure 4.21a by the presence of overlapping grains of approximately $0.08\text{-}0.1 \text{ }\mu\text{m}$ radius. After *ca.* 50% sulfidation, large agglomerates ($1\text{-}2 \text{ }\mu\text{m}$ diameter) are present due to the overlapping of the product layer (Figure 4.21b). As shown in Figure 4.22, these agglomerates are composed of closely packed grains ($0.05\text{-}0.1 \text{ }\mu\text{m}$ radius). Surface area measurements were also performed on ZnO sulfided at 400°C to determine whether the observed reduction in surface area is due to sintering or overlapping of the product layer. At this low temperature (400°C), sintering is negligible. The measured surface area for ZnO 50% sulfided is $2.4 \text{ m}^2/\text{g}$. Comparatively, at 650°C , the surface area for ZnO 50% sulfided is $2.0 \text{ m}^2/\text{g}$, i.e., some sintering takes place at 650°C .

The SEM photographs of unreacted ($2.3 \text{ m}^2/\text{g}$) and 90-95% sulfided Z2T3-a are shown in Figure 4.23a and 4.23b, respectively. The unreacted Z2T3-a is composed of small spherical grains (*ca.* $0.09 \text{ }\mu\text{m}$ radius), as well as larger plate-like grains (*ca.* $0.8\text{-}1.2 \text{ }\mu\text{m}$ length, not shown in the figure). EDS elemental analysis of the surface in Figure 4.23a estimates a ratio of $(\text{Zn}/\text{Ti})_{\text{atomic}} = 0.77$. This is more enriched in zinc than expected from stoichiometry ($\text{Zn}/\text{Ti} = 0.67$). After sulfidation, as shown in Figure 4.23b, a few large

a) unreacted ZnO

b) 54% sulfided ZnO

Figure 4.21 SEM micrographs of a) unreacted ZnO (calcined at 720°C) and b) 54% sulfided ZnO at 650°C in 2% H₂S-1% H₂-97% N₂.

a) 15000x

b) 30000x

Figure 4.22 SEM micrographs of 75% sulfided ZnO a) 15000x and b) 30000x.

a) 5000x

b) 10000x

Figure 4.23 SEM micrographs of a) unreacted Z2T3-a (calcined at 720°C) and b) ~90-95% sulfided Z2T3 at 650°C in 2% H₂S-1% H₂-97% N₂.

c) 5000x

d) 10000x

Figure 4.23 SEM micrographs at higher magnification of large
(cont'd.) agglomerates observed in Figure 4.23b. c) agglomerate
in upper portion and d) agglomerate in lower portion
of Figure 4.23b.

growths were present on the surface. Small dispersed grains composed mainly of TiO_2 ($\text{Zn/Ti} = 9 \times 10^{-2}$ and $\text{S/Zn} = 0.94$) covered the remaining surface shown in Figure 4.23b. Figure 4.23c shows a magnification of the growth in the upper portion of Figure 4.23b, while Figure 4.23d is a magnification of the agglomerate in the lower portion of that photograph. In Figure 4.23c, flat grains ($0.08\text{--}0.14 \mu\text{m}$ radius), are distinguishable with a composition of $(\text{Zn/Ti})_{\text{atomic}} = 0.32$ and $(\text{S/Zn})_{\text{atomic}} = 1.0$. The agglomerate of Figure 4.23d appears more sintered; individual grains are fused to one another. This agglomerate contains much less titanium, i.e. $(\text{Zn/Ti})_{\text{atomic}} = 1.8$ and $(\text{S/Zn})_{\text{atomic}} = 1.0$. Therefore, while ZnS tended to sinter, TiO_2 inhibited this sintering by acting as a physical barrier to prevent coalescence of ZnS. Regions with high titanium content preserved small grain sizes, thus keeping agglomerates from forming and growing.

4.3.4 Effect of H_2

Comparative plots of the initial reduction rate (shown in Section 3) and the initial sulfidation rate are depicted in Figure 4.24. The reduction rate is shown for a gas containing 2 mol% H_2 -98 mol% N_2 at 700°C . The reduction rate was calculated from the kinetic constants obtained in Section 3. The sulfidation rate is shown for a gas containing 2 mol% H_2S -1 mol% H_2 -97 mol% N_2 at 700°C . As will be discussed below, eliminating the 1 mol% H_2 from the reactant gas caused no significant change in the initial sulfidation rate. For single ZnO, the reduction rate is approximately 1.3 times higher than the sulfidation rate. However, for Zn-Ti-O sorbents reduction will occur at a much slower rate (about tenfold slower) than sulfidation.

Figure 4.25 shows comparative Arrhenius plots of the initial reduction and sulfidation

Figure 4.24 Comparative plots of the initial reduction and sulfidation rates.

Figure 4.25 Comparative Arrhenius plots of the initial reduction and sulfidation rates for ZnO, Z2T-a and Z2T3-a sorbents.

rates for the sorbents ZnO, Z2T-a and Z2T3-a. The reduction rate is shown for a gas containing 10% H₂-3% H₂O-87% N₂, while sulfidation is for 2% H₂S-98% N₂. The cross-over temperature at which the initial reduction rate became faster than the initial sulfidation rate was 848, 872 and 942°C, respectively for ZnO, Z2T-a and Z2T3-a sorbents. Consequently, Zn-Ti-O solids can be used for the desulfurization of coal-derived gas at higher temperatures than ZnO. The higher operating temperature largely compensates for the lower rate of sulfidation of Zn-Ti-O solids relative to that of ZnO.

No change in the initial sulfidation rate was observed with the addition of various amounts of H₂ (0, 1, and 10%) in the gas stream at temperatures in the range of 400-800°C. The conversion profiles after the initial sulfidation period were also not affected by varying the amount of hydrogen in the gas. This is shown in Figure 4.26 for the sorbents ZnO, Z2T-a, and Z2T3-a at sulfidation temperatures of 500 and 700°C.

The fact that no significant difference in the initial sulfidation rate was observed with 0% H₂ or 10% H₂ at various temperatures appears to contradict the results shown in Figure 4.24, namely that the ZnO reduction rate (with H₂ and N₂) is comparable to its sulfidation rate. Thus, significant zinc loss should have occurred during sulfidation in 2 mol% H₂S-10 mol% H₂-88 mol% N₂ at 700°C. However, the reason that no zinc loss (within 5%) was measured in the TGA is because zinc vapor diffusing out of the particle would react with H₂S to form ZnS. After reaction, a faint white film was observed on the quartz pan. Analysis of the film by atomic absorption spectroscopy identified the presence of zinc. The formation of the film is likely due to reaction of (escaped) Zn(g) formed by reduction of the sorbent and H₂S. Figure 4.27a shows small, spherical crystals formed as a result of the

Figure 4.26 Conversion profiles with various hydrogen concentrations at a) 500°C and b) 700°C.

Figure 4.27 SEM micrographs of sorbent Z2T-a showing a) crystals formed by the gas-phase $\text{Zn-H}_2\text{S}$ reaction at 700°C in $2\%\text{H}_2\text{S}-10\%\text{H}_2-88\%\text{N}_2$ and b) surface after 10% reduction at 700°C in $10\%\text{H}_2-90\%\text{N}_2$.

reaction of H_2S with Zn vapor leaving the sorbent Z2T-a from a crater-like hole on the surface. Figure 4.27b shows the same sorbent after 10% reduction in 10 mol% H_2 -90 mol% N_2 . Holes are present on the surface where Zn vapor had escaped. Consequently, desulfurization in a reducing atmosphere with ZnO can proceed along two parallel routes. Firstly, there is the direct sulfidation of solid ZnO

Secondly, there is the gas phase sulfidation of zinc vapor produced by reduction of ZnO

Typical sulfidation profiles for ZnO and Z2T-a at 800°C with various hydrogen amounts (1, 10, and 20 mol%) are shown in Figure 4.28. For both ZnO and Z2T-a, no zinc loss was evident in the TGA experiments. Both sorbents were completely sulfided (based on the initial sorbent weight). Although little noticeable zinc loss took place, ZnO reduction did occur, but zinc vapor was fixed on the sorbent and the pan via reaction (4.16). Figure 4.28a shows that up to approximately 50% conversion, the reaction rates of ZnO stayed relatively constant with different gas compositions. Above 50% conversion, however, the reaction rate dropped when sulfidation was performed with a gas containing either 10 or 20% H_2 . When sulfidation was performed with 1% H_2 , the rate remained relatively constant until approximately 70% conversion where it dropped off. A possible explanation for the faster decrease of the reaction rate with 10 or 20% H_2 is pore blockage due to the deposition of solid product from the vapor phase reaction between $\text{Zn}(g)$ and $\text{H}_2\text{S}(g)$. Small

Figure 4.28 Effect of H_2 on the sulfidation conversion profiles at 800°C for a) ZnO and b) Z2T-a.

jumps seen occasionally in the sulfidation profiles (e.g. Figure 4.28 a, b) are believed to be due to the formation of cracks in the product layer. As the sulfidation product layer is formed, zinc and water vapor products will accumulate in the particle until the pressure is sufficiently high to cause the product layer to crack. At that point, reaction will occur rapidly, as indicated by the "jump" in the conversion profile. Since this effect (i.e. the jump) is relatively small, SEM micrographs of solids reacted prior to the jump and beyond it could not conclusively verify this explanation.

SEM micrographs of ZnO reacted at 800°C in various amounts of H₂ at 800°C are shown in Figure 4.29. Also shown in Figure 4.29 is the unreacted solid. With 2% H₂S-10% H₂-88% N₂, small ZnS crystals (0.05-0.2 μm radius) formed as the reaction of Zn(g) with H₂S(g) were deposited on the original surface (Figure 4.29b). In addition, large cracks are evident in several particles. One such crack is seen traversing the length of the picture shown in Figure 4.29b. These cracks were probably caused by interior pressure buildup leading to Zn(g) and H₂O(g) escaping from the particle. As shown in Figure 4.29a, small crystals and cracks were absent in the unreacted solid. Thus, for ZnO, reduction can cause not only zinc loss but also weakening in the strength of the material by crack formations and the formation of fine particles. With high H₂ content (20 mol%), similar features were observed on the ZnO surface as those shown for reaction with 10% H₂. A larger number of crystal formations due to the reaction of Zn(g) and H₂S(g) were observed. Moreover, as shown in Figure 4.29c, large spherical agglomerates (0.7-1.3 μm radius) were also observed on the surface of several of the examined particles. The agglomerates were composed of smaller crystals (ca. 0.04 μm radius). Apparently, the higher zinc vapor

a)

b)

Figure 4.29 SEM micrographs showing the effect of H_2 on ZnO sulfidation at $800^\circ C$: a) unreacted ZnO; b) ZnO after complete sulfidation in 2% H_2S -10% H_2 -88% N_2 .

c)

Figure 4.29 SEM micrographs showing the effect of H_2 on ZnO sulfidation at $800^\circ C$: c) ZnO after complete sulfidation in 2% H_2S -20% H_2 -78% N_2 .

concentration during sulfidation reaction with 20% H_2 in the reactant gas led to enhanced sintering. Sainamthip and Amarkoon (1988) have also reported enhanced grain growth in zinc vapor for manganese zinc ferrite.

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 amounts (1-20 mol%). This is in agreement with our earlier finding that Zn-Ti-O sorbents were more resistive to reduction than ZnO. Figure 4.30 shows SEM micrographs of Z2T-a after sulfidation with increasing hydrogen content. For higher hydrogen concentrations, grain boundaries are more clearly seen. This is consistent with the reported zinc volatilization occurring preferentially along grain boundaries (Sainamthip and Amarakoon, 1988). More information on structural effects of hydrogen on the sulfidation of Zn-Ti-O sorbents can be found in Lew (1990).

The above observations offer interesting possibilities for reactor design. Desulfurization in a fixed-bed reactor will lead to zinc loss. Because of the axial concentration gradient of H_2S in the sorbent bed, a portion of the bed will be in contact with a H_2S -free reducing gas (Figure 4.31). In this part of the bed, zinc loss can occur. On the other hand, desulfurization in a fluidized bed reactor offers the possibility of eliminating zinc loss. The disadvantages of this reactor configuration, however, are lower H_2S removal efficiency (due to bubbling) as well as the fact that vapor phase reaction between H_2S and Zn will produce fines and lead to sorbent loss and elutriation. For the fluidized bed reactor, mixed Zn-Ti oxides would still be preferable as sulfur sorbents over ZnO because of lower particle disintegration (due to crack formation) and lower production of fines.

Figure 4.30 SEM micrographs showing the effect of H_2 on Z2T-a sulfidation at $800^\circ C$:
 a) Z2T-a after complete sulfidation in 2% H_2S -1% H_2 -97% N_2 ; b) Z2T-a after complete sulfidation in 2% H_2S -10% H_2 -88% N_2 .

Figure 4.30 SEM micrographs showing the effect of H_2 on Z2T-a sulfidation at $800^\circ C$:
(cont'd.)
c) Z2T-a after complete sulfidation in 2% H_2S -20% H_2 -78% N_2 .

Figure 4.31 Desulfurization in a fixed-bed reactor.

4.3.5 Effect of H₂O

The next parameter investigated in Zn-Ti-O sulfidation was H₂O. As discussed in Section 3, the presence of water vapor has the beneficial effect of significantly inhibiting the reduction of ZnO and subsequent zinc loss. Water vapor was added to the reactant gas stream to examine whether any effects similar to those found in reduction may also be present in sulfidation.

Experiments were performed in a gas mixture consisting of 2 mol% H₂S-1 mol% H₂O-1 mol% H₂-96 mol% N₂. For these experiments, a nitrogen-hydrogen gas stream was saturated with water vapor at room temperature (25°C). The saturated gas stream and a H₂S-N₂ stream were mixed and entered the reactor through a side arm. Nitrogen was also continuously passed into the balance to prevent the corrosive gas from reaching the balance mechanism. When water vapor is absent from the reactant gas stream, the calculated concentration of H₂O (produced during sulfidation) in the external film of the particle is approximately zero. Therefore, although the 1 mol% H₂O used here is a smaller amount than what is typically found in coal-derived fuel gases (e.g. 50 mol% from a fixed-bed Lurgi gasifier and 10 mol% from a fluidized-bed KRW gasifier; values from Halow, 1986), it is much higher than what can be found in the external film. Thus, any inhibition effect that water vapor may have on sulfidation should be readily apparent in a gas containing 1 mol% H₂O.

The conversion profiles of ZnO, Z2T-a, Z2T3-a were examined. As illustrated in Figure 4.32, no significant effect was observed by the presence of water vapor at either 400 or 700°C. Thus, no inhibition effects on either the initial sulfidation rate or diffusion

Figure 4.32 Comparison of conversion profiles for various sorbents reacted in 2% H_2S -1% H_2O -1% H_2 -96% N_2 and 2% H_2S -1% H_2 -97% N_2 at a) 400°C and b) 700°C . (Data points for reaction in H_2O)

through the sulfidation product layer were present when 1 mol% H_2O was added to the reactant gases. While the presence of water vapor can significantly change the initial reduction rate, no such effect was found in sulfidation. From the results of sulfidation experiments with H_2O , some indications of the reaction sites involved in sulfidation can be drawn. Two types of sites (Type A and B) were identified in reduction of ZnO . Type A sites were found to be poisoned by H_2O and H_2S . Type A sites, thus, were not involved in sulfidation. The number of type B sites was found to decrease with increasing relative amount of TiO_2 in the sorbent. However, no decrease in the initial sulfidation rate was observed when the relative amount of TiO_2 was increased from 25 mol% to 60 mol%. Thus, Type B sites were also not involved in sulfidation. Consequently, reduction and sulfidation must proceed on different reaction sites, independent of each other.

Although there were no discernible differences in the sulfidation profiles of different sorbents with the addition of water vapor, it was observed that water vapor enhanced the sintering of the sorbent. The surface areas of a few reacted sorbents were measured to determine the extent of sintering which occurred in the presence of water vapor. These results are shown in Figure 4.33. For ZnO , after *ca.* 90% sulfidation, the surface area decreased 43% from its original value. In contrast, in the absence of H_2O , the surface area decreased only 29%. Sorbent Z2T3-a for which an increase of surface area (20%) takes place after dry sulfidation, showed only 11% increase in surface area in wet sulfidation.

4.3.6 Regeneration of Bulk Zn-Ti-O Sorbents

In order for Zn-Ti-O solids to be used commercially for desulfurization of hot fuel gases, the sulfided solids must be regenerable. To determine the regenerability of Zn-Ti-O

Figure 4.33 Surface area change after sorbent sulfidation at 650°C in the presence and in the absence of water vapor.

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 4.34 in terms of the dimensionless weight W/W_o (where W is the instantaneous and W_o is the initial weight of the solid) versus the reaction time. Prior to the first cycle, the solids were reduced in 10% H_2 -90% N_2 for seven minutes. The partially reduced solids were then sulfided in 2% H_2S -98% N_2 . After sulfidation, regeneration was performed in air. All reactions were run at 650°C.

As discussed previously, the decrease of sulfidation rate of sorbent Z2T-a at high conversion, seen in Figure 4.34, was due to non-uniform grain size distribution in the solid. In the first cycle, regeneration of Z2T-a and ZnO was essentially complete after 40-50 minutes. Based on the final weight after regeneration, little if any zinc sulfate ($ZnSO_4$) was formed during regeneration. In the second cycle, the sulfidation performance of ZnO was slightly worse than that in the first cycle. As shown in Figure 4.34, the sulfidation rate in cycle 2 decreased noticeably after approximately 90% conversion ($W/W_o=1.06$). By contrast, the sulfidation of Z2T-a in cycle 2 was the same as in the first cycle. The second regeneration was slightly slower than the first for both Z2T-a and ZnO, reaching about 95% completion after 40-50 minutes.

4.4 SUMMARY/CONCLUSIONS

--The initial sulfidation rate of Zn-Ti-O sorbents measured with 90-125 μm particles in the TGA was found to be 1.5-2 times slower than that of ZnO. At temperatures between 400-700°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 Zn-Ti-O sorbents.

Figure 4.34 Sulfidation-regeneration cycles of
 a) ZnO and b) Z2T-a. 1. Reduction
 in 10% H_2 -90% N_2 ; 2. Sulfidation in
 2% H_2S -98% N_2 ; 3. Regeneration in
 21% O_2 -79% N_2 .

Therefore, it is proposed that 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 further decrease of the frequency factor.

--Similar sulfidation kinetics were measured for the different zinc titanate phases (i.e. Zn_2TiO_4 , $\text{Zn}_2\text{Ti}_3\text{O}_8$, and ZnTiO_3).

--The presence of titanium in ZnO was found to inhibit sintering of ZnS. In fact, Zn-Ti-O sorbents showed a measurable 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. 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 $\text{H}_2\text{S(g)}$ to form fine particles of ZnS(s) . Such structural effects were largely absent from the surface of Z2T-a particles after reaction at the same conditions as ZnO.

--No effect of water vapor on the sulfidation kinetics was observed for temperatures in the range of 400-700°C. However, the presence of H_2O enhanced the sintering of both ZnO and Zn-Ti-O sorbents.

--Zn-Ti-O sorbents allow raising the operating temperature for fuel gas desulfurization as a result of their lower reduction rate. For example, a solid with

$(\text{Zn/Ti})_{\text{atomic}} = 2/3$ can operate at a sulfidation temperature 94 degrees Celsius higher than for ZnO. This higher operating temperature compensates for the decrease in the sulfidation rate of ZnO upon addition of TiO_2 .

As an overall conclusion, therefore, the choice of sorbent composition for desulfurization should be based on the extent of solid reduction tolerated and the sulfur loading desired. In the absence of H_2O , the best sorbent composition for operation in a fixed-bed reactor is one with a ratio of $(\text{Zn/Ti})_{\text{atomic}} \approx 3/1$. A higher percentage of titanium produces no improvement in suppressing the zinc loss, while it decreases the attainable sulfur loading. However, in the presence of H_2O or for operation in a fluidized bed reactor, a higher percentage of titanium is needed in order to decrease the reduction rate. This will be at the expense of sulfur loading. For example, a solid with $(\text{Zn/Ti})_{\text{atomic}} = 2/3$ which has nine times lower reduction rate than ZnO, also has 2.25 times lower sulfur loading than ZnO, namely, *ca.* 0.15 g sulfur/g sorbent (based on complete conversion to ZnS and TiO_2).

5. MODELING OF SULFIDATION

5.1 BACKGROUND

Various mathematical models have been presented in the literature for gas-solid reactions. They can generally be classified as either grain models representing the structure as an assemblage of very small grains, usually spherical in shape, or as pore models representing the porous solid by a collection of capillaries. As would be expected, very different reaction profiles are calculated depending on the structural model employed.

One of the earliest gas-solid reactions model described a solid with overlapping pores of uniform size randomly distributed in space (Petersen, 1957). Further refinements of the model were introduced to more closely describe the physical structure of the solid. This model was extended to include the possibility of solid product formation which changes the surface area and porosity of the solid (Cavelo and Cunningham, 1970; Ramachandran and Smith, 1977[1]). Recently, the model was expanded to describe a pore size distribution with randomly overlapping pores (Gavalas, 1980; Bhatia and Perlmutter, 1980; Bhatia and Perlmutter, 1983). Concurrently, variable property grain models allowing for solid product formation and sintering have also been proposed (Hartman and Coughlin, 1976; Szekely, 1976; Georgakis et al., 1979; Ramachandran and Smith, 1977[2]; Ranade and Harrison, 1981). In these models, the solid was represented by non-overlapping, uniform size grains. Several different grain shapes (e.g. spheres, plates, and cylinders) were used. More recently, an overlapping grain model with a grain size distribution was developed for gas-solid reaction (Sotirchos and Yu, 1988). To facilitate this discussion, the non-overlapping grain

model will be designated as the grain model while the overlapping one will be called the random grain model.

The fundamental difference between the pore model and grain model is in the representation of the solid structure, its reactant surface area, and its pore surface area. General schematic representations for the random pore, grain and random grain models are shown in Figure 5.1. The reactant surface area will influence both the rate of chemical reaction as well as the diffusion through the product layer. The pore surface area will only affect the product layer diffusion. The random pore model and grain model give very different expressions for the reactant and pore surface area, and this will correspondingly affect the reaction profile. The grain model predicts a monotonically decreasing surface area ($S(X)$) with increasing conversion for spherical and cylindrical shape grains:

$$S^*(X) = (1-X)^m \quad (5.1)$$

where $S^*(X)$ is the normalized reaction surface area [$S(X)/S_0$], m is the shape factor (sphere = 2/3; cylinder = 1/2), and X is the fractional conversion. $S(X)$ is the reaction surface area per unit volume and S_0 is the surface area per unit volume at $X=0$. For flat plate, the reaction surface area remains constant with conversion.

The random pore model is more versatile in describing the reaction surface area because with certain values of the structural parameters, it is possible to observe a maximum in the surface area. Some systems, such as the gasification of coal and char have been known to exhibit a maximum in the reaction rate (Dutta et al., 1977; Dutta and Wen, 1977), which has been attributed to a maximum in the reaction surface area. This maximum can arise from two opposing effects: (1) the growth of the reaction surface as the pore radius

a) Random Pore Model with a distributed pore size
(from Bhatia and Perlmutter, 1980)

b) Grain Model

c) Random Grain Model
(uniform spherical grains)

● unreacted solid

Figure 5.1 Schematic representations of the reacting porous solid by a) random pore b) grain and c) random grain models.

increases and (2) the decrease in reaction surface as pores progressively collapse by intersection. For the random pore model with uniform cylindrical pores, the reaction surface area is

$$S^*(X) = (1-X)\sqrt{1-\psi\ln(1-X)} \quad (5.2)$$

where ψ is a structural parameter equal to $4\pi L_{E0}/S_{E0}^2$, L_{E0} is the total length of non-overlapping cylindrical surface per unit volume at $t=0$, and S_{E0} is the surface area per unit volume at $t=0$. Depending on the value of ψ , a maximum may be present in the value of $S^*(X)$.

Like the reaction surface area, the expressions for the pore surface area are very different for the random pore and the grain model. For the grain model, the pore surface area is

$$S_p^*(X) = [1+(Z-1)X]^m \quad (5.3)$$

For the random pore model, it is

$$S_p^*(X) = [1+(Z-1)X]\sqrt{1-\psi\ln(1+(Z-1)X)} \quad (5.4)$$

where Z is the volume of product formed per unit volume of reactant. The grain model produces the anomaly of a monotonically increasing pore surface area even when the porosity reduces to zero. This produces a discontinuity in the reaction profile at the point where the porosity reaches zero. On the other hand, the random pore model more realistically predicts that as the porosity goes to zero the pore surface area also goes to zero. The porosity is customarily assumed to vary linearly with conversion according to

$$\varepsilon = \varepsilon_0 - (1 - \varepsilon_0)(Z - 1)X \quad (5.5)$$

Due to the inadequacies of the grain model in certain areas (e.g. reaction and pore surface area prediction), further refinements of the model were developed. One basic problem with the grain model is the assumption that the individual grains grow independently with no overlapping. This would be true for $Z \leq 1$ or very porous material (ε_0 large). To obtain a more realistic and flexible model, Lindner and Simonsson (1981) in their partially sintered sphere model (PSSM) represented the initial solid structure as an aggregate of truncated spheres (i.e. overlapping spheres) in contact with each other in an initial stage of sintering. In the PSSM-model, the pore reaction surface area tends to zero with decreasing porosity. Depending on the values of the structural parameters, λ (initial degree of sintering of spheres estimated from microscopic pictures of the solid structure) and ε (porosity), the PSSM-model can predict an initial increase of the reaction surface area with conversion. In general, however, the degree of overlapping of spheres is not uniform throughout the solid structure. Thus, one value for λ cannot be used. Sotirchos and Yu (1988) further refined this model by allowing grains of different shapes (e.g. sphere, cylinder, and plate) to randomly overlap with each other. Since many solid structures do not have a uniform grain size, these authors also allowed for the possibility of a grain size distribution. The resulting expressions obtained for the reaction and pore surface area are

$$S^* = \frac{\varepsilon_r \int_{r(0)}^{r_{0,\max}} r_r^{F_s-1} n_0(r_0) dr_0}{\varepsilon_0 \int_{r_{0,\min}}^{r_{0,\max}} r_0^{F_s-1} n_0(r_0) dr_0} \quad (5.6)$$

$$S_p^* = \frac{\epsilon_p \int_{r_{0,\min}}^{r_{0,\max}} r_p^{F_g-1} n_0(r_0) dr_0}{\epsilon_0 \int_{r_{0,\min}}^{r_{0,\max}} r_0^{F_g-1} n_0(r_0) dr_0} \quad (5.7)$$

where

ϵ_r = porosity of reactant solid

ϵ_p = porosity of porous solid (reactant+product)

r_0 = initial grain size (radius for spheres and cylinders or half-thickness for plate)

$r_{0,\max,\min}$ = initial upper and lower limit of grain size range

$r_{r,p}$ = size of grain of initial size r_0 at the reactant (r) and pore surface (p)

at time t

$Y(t)$ = lower limit of active grain size range

$n_0(r_0)dr_0$ = number of grains per unit volume with size in the initial size range

$[r_0, r_0 + dr_0]$

F_g = grain shape factor (3 for a sphere, 2 for a cylinder, and 1 for a plate)

A better description of the solid structure is obtained with this model than with the grain model. The overlapping grain (random grain) model is more flexible and powerful than the grain model in that it can predict various behaviors (e.g. a maximum in the rate-conversion profile). This type of model has been successful in predicting the deactivation in hydrodemetallation catalysts (Van Eekelen, 1973; Smith, 1988). However, as with all models which try to closely approximate realistic behavior, the computational complexity of the random grain model is greater than that of the grain model.

In this project, extensive SEM analysis of the fresh sorbents used in sulfidation

experiments (e.g. Figures 4.12, 4.15, 4.21 and 4.23) showed that the solids would be more closely described as aggregates of individual grains rather than as a solid structure with well-defined pores. Modeling of the sulfidation of these systems was, therefore, undertaken with the grain model. In comparison, the random grain model was also used to examine whether it could better predict the experimental reaction profiles. Results from this analysis are presented in the following sections.

5.2 THE GRAIN MODEL

Various desulfurization systems have been modeled with the grain model. Gibson and Harrison (1980) and Ranade and Harrison (1981) used the grain model to describe the ZnO-H₂S reaction system. The Fe₂O₃-H₂S system was also analyzed with the grain model (Tamhankar et al., 1981). The resistances in the latter system were due to chemical reaction and pore diffusion and, thus, application of the constant property (i.e. no structural changes due to reaction and/or sintering) grain model was good. For the ZnO-H₂S system poorer agreement with the constant property grain model was observed (Gibson and Harrison, 1980) which was later improved by incorporating structural changes due to reaction and sintering (Ranade and Harrison, 1981).

The gas-solid sulfidation reaction can be represented by the general stoichiometry

The solid reactant is visualized as being composed of a large number of non-porous grains of regular geometry (i.e. sphere, cylinder, or plate). Each grain reacts like a shrinking core. As the reaction proceeds, the unreacted core decreases in size while maintaining its original geometric shape. Around the unreacted core, a solid product layer which may be porous

or nonporous is developed. Depending on the relative density of the solid product and reactant, the overall size of the grain may change.

There are several possible resistances to the gas-solid reaction rate, such as resistances due to mass transfer, pore diffusion, product layer diffusion, and chemical (surface) reaction. In the experiments performed in this study, both mass transfer and pore diffusional limitations were eliminated by suitable choices of gas flowrate, sample quantity, and particle size and macroporosity. Only product layer diffusion and chemical reaction resistances were important.

The expressions derived for the grain model (Szekely et al., 1976) are based on the assumptions of: 1. isothermal reaction; 2. first order intrinsic reaction rate with respect to gas concentration; 3. irreversible reaction; 4. equimolar counter-diffusion; 5. pseudo-steady state approximation; and 6. structural changes due only to reaction (i.e. no sintering). The following expression is derived for the case when both product layer diffusion and chemical reaction control the rate:

$$t^* = g_{Fg}(X) + \sigma_s^2 p_{Fg}(X) \quad (5.9)$$

where

t^* = dimensionless time

$$= \left(\frac{bk}{\rho_s r_o} \right) C_{A_s} t \quad (5.10)$$

$g_{Fg}(X)$ = resistance due to chemical reaction

$$= 1 - (1-X)^{1/Fg} \quad (5.11)$$

$p_{F_g}(X)$ = resistance due to diffusion through the product layer

$$= 3 \left\{ \frac{Z - [Z + (1-Z)(1-X)]^{2/3}}{Z-1} - (1-X)^{2/3} \right\}_{\text{sphere}} \quad (5.12)$$

$$= \frac{[Z + (1-Z)(1-X) \ln[Z + (1-Z)(1-X)]]}{Z-1} + (1-X) \ln(1-X)_{\text{cylinder}} \quad (5.13)$$

$$= ZX^2, \text{ plate} \quad (5.14)$$

σ_s^2 = product layer diffusion resistance/chemical reaction resistance

$$= k r_o / 2 F_g D_e \quad (5.15)$$

$$r_o = \frac{F_g}{A_{os} \rho_s} \quad (5.16)$$

where k is the intrinsic rate constant (cm/s); ρ_s is the solid reactant density (mmol/cm³); r_o is the initial grain radius (initial half-thickness for plate) (cm); A_{os} is the initial specific surface area (cm²/mmol); C_{Ao} is the concentration of the gaseous reactant in the bulk gas (mmol/cm³); F_g is the shape factor (3=sphere; 2=cylinder; 1=plate); Z is the ratio of the product to reactant molar volume; and D_e is the product layer diffusion coefficient (cm²/s).

The sulfidation conversion profiles of several Zn-Ti-O and ZnO sorbents were analyzed with the grain model. This analysis was aimed at understanding the role of TiO₂ at high sorbent conversions. Consequently, it was necessary to determine the effect of TiO₂ on the product layer diffusion. The diffusion coefficient (D_e) was the fitting parameter in this model. The values of k , the intrinsic rate constant, were obtained from the Arrhenius constants (Table 4.4) calculated from initial rate experiments. The sulfidation data were

obtained from experiments conducted with 2 mol% H_2S -1 mol% H_2 -97 mol% N_2 . Experimental data with higher concentrations of H_2 were not used for this part of the study because at higher temperatures (e.g. 800°C) the vapor phase reaction between Zn and H_2S can result in pore plugging. This can lead to an unexpected decrease in the reaction rate.

A comparison of the experimental results and the predicted conversion profiles is shown in Figures 5.2 and 5.3 for ZnO at low ($400\text{--}600^\circ\text{C}$) and high ($700\text{--}800^\circ\text{C}$) temperatures. The values of the parameters used in the model are listed in Table 5.1. Also listed in Table 5.1 are the calculated diffusion coefficients. The grains were assumed to have a spherical shape ($F_g=3$), which was confirmed after examining the material under a scanning electron microscope. The initial grain radius was calculated from Eq. (5.16) for $F_g=3$.

However, the calculated grain radius was larger than the grain radius measured by analyzing SEM micrographs of ZnO (Figures 4.12 and 4.21). Figure 5.4a shows the grain size distribution of ZnO (surface area = $2.41\text{ m}^2/\text{g}$, calcined at 720°C for 4 h) measured from SEM micrographs. The discrepancy between the calculated and measured grain radii was even greater with more sintered materials. Figure 5.4b shows the grain size distribution of ZnO (surface area = $1.33\text{ m}^2/\text{g}$) calcined at the same temperature for a longer period of time (12 h). The calculated grain radius was $0.40\text{ }\mu\text{m}$ while the measured grain size distribution had a peak centered at *ca.* $0.15\text{ }\mu\text{m}$. The SEM micrograph of this sintered ZnO is shown in Figure 5.5. The solid structure is characterized by overlapping grains which causes the error in the calculated grain radius.

At 400°C ($\sigma_s^2 \geq 10$), the system was controlled by the diffusion through the product

Figure 5.2 Comparison of experimental sulfidation profiles of ZnO at 400-600°C (2%H₂S-1%H₂-97%N₂) with calculated profiles from grain model.

Figure 5.3 Comparison of experimental sulfidation profiles of ZnO at 700 and 800°C (2%H₂S-1%H₂-97%N₂) with calculated profiles from the grain model.

**Table 5.1 Parameter values used to calculate ZnO conversion profiles in
Figures 5.2 and 5.3**

$A_{0,s}$ (surface area, cm^2/mmol)	1961
ρ_s (density, mmol/cm^3)	68.9
k (rate constant, cm/s)	$1.3\exp[-10.3\text{kcal}/\text{mol}/RT]$
Molar Gas Composition	2% H_2S -1% H_2 -97% N_2
Z	1.64
F_g	3
b	1
De (cm^2/s) - 400°C	3.8×10^{-10}
500°C	3.5×10^{-9}
600°C	3.5×10^{-8}
700°C	3.0×10^{-7}

Figure 5.4 Grain size distribution of a) ZnO, 2.41 m²/g and b) ZnO, 1.33 m²/g. (Comparison with the grain model)

Figure 5.5 SEM micrograph of ZnO calcined at 720°C, 12 h. (Surface area: 1.33 m²/g)

layer except during the initial period of the reaction. At 500 and 600°C, both chemical reaction and product layer diffusion were controlling. Chemical reaction alone controlled the system at 700 and 800°C ($\sigma_s^2 < 0.1$).

The agreement between the predicted and the experimental sulfidation profiles for ZnO (Figures 5.2 and 5.3) was quite good at temperatures up to 700°C considering that the reduction in surface area due to the overlapping of product layer and sintering was ignored in the model. However, the grain model predicted an increasing surface area with sulfidation, while the experimental results found a decrease in the surface area for sulfidation at 650°C (Figure 5.6). Sintering appears to have no effect on the conversion profiles as indicated by the relatively good fit between the model prediction and the experimental profiles at 650°C where limited sintering takes place. However, at this temperature, the product layer diffusion resistance has a relatively minor effect. Ranade and Harrison (1980) observed similar results with ZnO. When they incorporated sintering into the model, it had very little effect on the predicted time-conversion profiles, because at temperatures where sintering is important, grain diffusion resistance is negligible.

At 800°C, the model tends to underpredict the experimental results (Figure 5.3). At this temperature, however, there may be enhancement of the actual reaction rate by the homogeneous reaction, $\text{Zn(g)} + \text{H}_2\text{S(g)} = \text{ZnS(s)} + \text{H}_2\text{(g)}$ (discussed in Section 4).

The grain model was also used to describe the sulfidation of the Zn-Ti-O solids. The predicted values from the grain model and the experimental results for both sorbents Z2T-a (Figures 5.7 and 5.8) and Z2T3 (Figure 5.9) were not as close as for ZnO. Physical properties and product layer diffusion coefficients for the Zn-Ti-O sorbents are listed in

Figure 5.6 Comparison of the predicted surface area change from the grain model with the experimental data at 650°C (2% H₂S-1%H₂-97%N₂) for ZnO.

Figure 5.7 Comparison of experimental sulfidation profiles of Z2T-a at 400-600°C (2%H₂S-1%H₂-97%N₂) with calculated profiles from the grain model.

Figure 5.8 Comparison of experimental sulfidation profiles of Z2T-a at 700 and 800°C (2%H₂S-1%H₂-97%N₂) with calculated profiles from the grain model.

Figure 5.9 Comparison of experimental sulfidation profiles of Z2T3 at 400-700°C (2%H₂S-1%H₂-97%N₂) with calculated profiles from the grain model.

Table 5.2. The modeling was based on spherical grains. The calculated sulfidation profiles underpredicted the experimental results at low conversion and overpredicted them at higher conversion. Sintering was eliminated as a cause of this decrease in the reaction rate since the surface area of sulfided Z2T3 and Z2T-a sorbents changed only slightly from the fresh sorbent value.

The poor agreement between the grain model and the experimental results was due either to unaccounted intrinsic chemistry of the Zn-Ti-O system or to the physical properties of the material. The term intrinsic chemistry of the Zn-Ti-O system is used to indicate a potential decrease in the reaction rate after a certain extent of sulfidation similar in all Zn-Ti-O sorbents. This can occur by chemical phase change after a certain extent of sulfidation, e.g., to a much less reactive phase than the initial phase. During sulfidation, sorbent Z2T-a, which contained only the phase Zn_2TiO_4 , formed $\text{Zn}_2\text{Ti}_3\text{O}_8$ and ZnS. After 67% conversion, only the phases $\text{Zn}_2\text{Ti}_3\text{O}_8$ and ZnS were present. Experiments with Z2T-b were also performed. Z2T-b, like Z2T-a, contained only Zn_2TiO_4 . However, its physical properties were very different from Z2T-a. It was prepared with a higher surface area ($13.9 \text{ m}^2/\text{g}$) and had a more uniform grain size (Figure 4.15). As shown in Figure 5.10, the agreement between the calculated conversion profiles and the experimental results for Z2T-b was much better than for Z2T-a. The observed differences in the progress of reaction for Z2T-a and Z2T-b can then be attributed to the difference in their grain morphology (i.e. grain size distribution). Varying the grain size distribution has been shown to have a large effect on the conversion profile (Bartlett et al., 1973; Szekely and Propster, 1975; Sotirchos and Yu, 1988).

**Table 5.2 Parameter values used to calculate conversion profiles in Figures
5.7, 5.8 and 5.9**

Z2T

$A_{o,s}$ (surface area, cm^2/mmol)	9973
ρ_s (density, mmol/cm^3)	21.8
k (rate constant, cm/s)	$0.40\exp[9.3\text{kcal}/\text{mol}/RT]$
Molar Gas Composition	2% H_2S -1% H_2 -97% N_2
Z	1.45
F_g	3
b	0.5
De (cm^2/s) - 400°C	1.3×10^{-10}
500°C	6.7×10^{-10}
600°C	1.2×10^{-9}
700°C	5.0×10^{-9}

Z2T3

$A_{o,s}$ (surface area, cm^2/mmol)	9216
ρ_s (density, mmol/cm^3)	11.7
k (rate constant, cm/s)	$0.40\exp[9.3\text{kcal}/\text{mol}/RT]$
Molar Gas Composition	2% H_2S -1% H_2 -97% N_2
Z	1.22
F_g	3
b	0.5
De (cm^2/s) - 400°C	4.2×10^{-11}
500°C	6.0×10^{-10}
600°C	3.3×10^{-9}
700°C	1.5×10^{-8}

Figure 5.10 Comparison of experimental sulfidation profiles of Z2T-b at 400 and 500°C (2%H₂S-1%H₂-97%N₂) with calculated profiles from the grain model.

The grain model, although successful in predicting the conversion evolution of ZnO has several drawbacks. First, based on the assumption that the solid was composed of non-overlapping grains, the calculated grain radius was larger than the grain radius measured from SEM micrographs. The solid structures observed in the photographs were composed of overlapping grains. Second, it failed to predict the surface area changes observed for ZnO. The possibility of overlapping product layer which will decrease the surface area was not taken into account. Last, in order to model Zn-Ti-O solids such as Z2T-a and Z2T3, non-uniform grain sizes must be used.

5.3 THE RANDOM GRAIN MODEL

In order to more closely simulate the solid structure of ZnO and Zn-Ti-O, a random grain model was used. The porous solid is simulated as an assemblage of grains randomly distributed in space. The centers of the grains are randomly placed in space and overlapping of the grains is permitted. This is consistent with the observed solid structures of the sorbents studied in this project. If the solid product occupies more volume than a stoichiometrically equal volume of reactant, then overlapping of the product resulting in pore closure is possible. Contributions from particle sintering are ignored in using this model. Since the solid reactants were calcined at 720°C for 4-12 h, sintering of the reactants is minimal except at higher reaction temperatures where product layer diffusion is negligible.

Early models based on random grains were limited to only spherical grain shape (Weissberg, 1963; Haller, 1965; Van Eekelen, 1973). These models were further extended to include various grain shapes and solid product formation by Sotirchos and Yu (1988).

As discussed in Section 5.1, the porosity (ϵ) and the surface area (S) are uniquely defined by this model. The expressions for the initial porosity (ϵ_o) and the initial surface area per unit volume (S_o) of grains randomly distributed in space are:

$$\epsilon_o = \exp(-\phi_{ox}) \quad (5.17)$$

$$S_o = \epsilon_o S_{ox} \quad (5.18)$$

$$S_{ox} = F_g f \int_{r_{o,min}}^{r_{o,max}} r_o^{F_g-1} n_o(r_o) dr_o \quad (5.19)$$

$$\phi_{ox} = f \int_{r_{o,min}}^{r_{o,max}} r_o^{F_g} n_o(r_o) dr_o \quad (5.20)$$

where ϕ_{ox} and S_{ox} are the total volume and specific surface area (cm^2/cm^3) of grains at time t without correction for overlapping, respectively; F_g is the grain shape factor (sphere=3; cylinder=2; plate=1); r_o is the initial grain radius; f is the grain geometric factor (sphere= $4\pi/3$; cylinder= πL_{avg} ; plate= $2A_{avg}$), L_{avg} and A_{avg} are the average grain length of the cylinder and average grain surface area of plate-like grains, respectively; $n_o(r_o)dr_o$ is the number of grains per unit volume with size in the initial size range $[r_o, r_o + dr_o]$. The initial specific surface area (S_o) is obtained by the fact that the probability of any random point not lying within a grain is equal to the initial porosity (ϵ_o). Therefore, only a fraction (ϵ_o) of the surface (S_{ox}) has a probability of lying outside the solid volume.

For a reactive system, equations similar to Eq. 5.17-5.20 can be derived for both the reaction surface and the pore surface. The assumption was made that the number of grains per unit volume does not change with the reaction. For the reaction and pore surface at

time t , the expressions are

$$\varepsilon_r = \exp \left[-f \int_{r(0)}^{r_{\max}} r_r^{F_r-1} n_o(r_o) dr_o \right] \quad (5.21)$$

$$S_r = F_r f \varepsilon_r \int_{r(0)}^{r_{\max}} r_r^{F_r-1} n_o(r_o) dr_o \quad (5.22)$$

$$\varepsilon_p = \exp \left[-f \int_{r_{\min}}^{r_{\max}} r_p^{F_p-1} n_o(r_o) dr_o \right] \quad (5.23)$$

$$S_p = F_p f \varepsilon_p \int_{r_{\min}}^{r_{\max}} r_p^{F_p-1} n_o(r_o) dr_o \quad (5.24)$$

These expressions for the solid structure can then be incorporated into a rate expression to yield

$$\frac{dr_r}{dt} = \frac{\frac{-bkC_{Ao}}{\rho_s}}{1 + \frac{k}{D_s} \varepsilon_r^{F_r-1} \int_{r_r}^{r_r} \frac{dr}{\varepsilon_{r,p}(t') r^{F_r-1}}} \quad (5.25)$$

The change in the pore radius (r_p) is related to the reaction surface radius of the grain (r_r) by

$$\frac{dr_p}{dt} = - \frac{dr_r}{dt} \left[(Z-1) \frac{\varepsilon_r^{F_r-1}}{\varepsilon_p^{F_p-1}} \right] \quad (5.26)$$

The porosity of the solid (product + reactant) is found by

$$\varepsilon_p = \varepsilon_o - (Z-1)(\varepsilon_r - \varepsilon_o) \quad (5.27)$$

The fractional conversion is calculated with

$$X = \frac{\varepsilon_o - \varepsilon_p}{(Z-1)(1 - \varepsilon_o)} \quad (5.28)$$

Equations (5.25)-(5.28) can be used to model a gas-solid reaction system. Again, the effective product layer diffusion coefficient (D_e) is used as a fitting parameter. Different grain size distributions can be incorporated by varying $n_o(r_o)$. This model is much more flexible than the grain model because it can describe various grain structures. For example, with certain values of the physical parameters (i.e. ε_o and S_o), it can predict a maximum in the reaction rate associated with a maximum in the reaction surface area. With other values of the physical parameters, it can predict a monotonically decreasing reaction rate. However, this model involves solution of more complex equations than the grain model.

5.4 APPLICATION TO ZnO AND Zn-Ti-O SULFIDATION

5.4.1 ZnO Modeling

Based on SEM micrographs of ZnO, e.g. Figure 5.11, a uniform size of spherical grains was used in the random grain model. Using Eq. (5.17), the initial porosity of the system for spheres is

$$\varepsilon_o = \exp \left[-\frac{4}{3} \pi r_o^3 n_o \right] \quad (5.29)$$

The specific surface area is

Figure 5.11 SEM micrograph of ZnO calcined at 720°C, 4 h.

$$S_o = n_o 4\pi r_o^2 \epsilon_o \quad (5.30)$$

Using Eq. (5.29) and (5.30), the grain radius is uniquely defined as

$$r_o = - \frac{3\epsilon_o}{S_o} \ln \epsilon_o \quad (5.31)$$

The porosity was obtained from mercury porosimetry measurements. Based on SEM information of a cross-section of the sorbent (Figure 5.12), pores with radius greater than 1 μm were ignored. These pores were not produced by the space between randomly placed grains and would lead to an erroneously high calculated value for the grain radius.

A useful property which can be calculated with the random grain model for spherical mono-sized grains is the mean pore radius (r_m). Van Eekelen (1973) obtained an approximate relationship for the mean pore radius which is valid for porosity in the range $0.3 < \epsilon < 0.8$,

$$r_m = \frac{2\epsilon_o}{S_o} (1.32 - \epsilon_o) \quad (5.32)$$

The calculated mean pore radius for ZnO using the value of the physical properties values listed in Table 5.3 is 0.16 μm . In comparison, the measured value of the mean pore radius is 0.20 μm .

Modeling of the reaction between ZnO and H_2S was performed with the random grain model (Eq. 5.25-5.28) for spherical grains (Eq. 5.29-5.31). Table 5.3 lists the values of the physical properties for ZnO used in this model. The calculated initial grain radius was 0.16 μm . This was closer to the actual grain size (Figure 5.4a) than the value predicted by the grain model (0.22 μm). A comparison of the predicted reaction profiles with the experimental reaction profiles is shown in Figure 5.13. The values of the effective product

Figure 5.12 SEM micrographs of ZnO cross-sectioned (calcined 720°C, 4 h).

Table 5.3 Parameter values used to calculate ZnO conversion profiles in Figure 5.13

s_o (surface area, cm^2/cm^3)	5.54×10^4
ϵ_o (porosity)	0.59
ρ_s (density, mmol/cm^3)	68.9
k (rate constant, cm/s)	$1.3 \exp[-10.3 \text{ kcal/mol}/RT]$
Molar Gas Composition	2% H_2S -1% H_2 -97% N_2
Z	1.64
F_g	3
b	1
De (cm^2/s) - 400°C	2.7×10^{-10}
500°C	3.0×10^{-9}
600°C	2.0×10^{-8}
700°C	1.0×10^{-7}

Figure 5.13 Comparison of experimental sulfidation profiles of ZnO at 400-700°C (2% H₂S-1% H₂-97% N₂) with calculated profiles from the random grain model.

Figure 5.14 Comparison of the surface area variation predicted by the random grain model and the grain model with the experimental results of ZnO sulfidation at 650°C (2% H₂S-1% H₂-97% N₂).

layer diffusion coefficients used in the calculation are listed in Table 5.3.

Unlike the grain model, the random grain model predicted a decreasing surface area with conversion. This was due to overlapping of the product layer. The decrease in surface area was in agreement with the measured value of the surface area after sulfidation at 650°C. Figure 5.14 shows the predicted change in surface area associated with the reaction for both the random grain model and the grain model. In addition, the effective diffusion coefficients calculated for ZnO using the random grain model were slightly smaller than the values found using the grain model. Although the predicted decrease in surface area with conversion in the random grain model would increase the predicted diffusion coefficient in comparison to the grain model, the smaller predicted initial grain radius has the opposite effect and would decrease the diffusion coefficient.

The predicted sulfidation profiles using the value of D_e calculated from the experiments performed with 2 mol% H_2S -1 mol% H_2 -97 mol% N_2 agree very well with the experimental profiles obtained with various H_2S concentrations as shown in Figure 5.15. This indicates that the assumption that the H_2S bulk concentration was equal (or proportional) to the concentration of the species diffusing through the product layer was correct. Eq. 5.25 was derived on the assumption that the driving force for diffusion is $(C_{A0} - C_{As})$ where C_{A0} and C_{As} are the concentrations of H_2S in the bulk gas and at the reaction interface, respectively. However, for solid state diffusion, the driving force should be $(C_{i,0} - C_{i,s})$ where $C_{i,0}$ and $C_{i,s}$ are the concentrations of the diffusing ion at the gas-solid and the reaction interface, respectively. Based on Figure 5.15, the ionic concentration gradient is proportional to the H_2S gradient.

Figure 5.15 Comparison of experimental sulfidation profiles of ZnO reacted at 500°C in 1, 2 and 3% H₂S with calculated profiles from the random grain model.

5.4.2 Zn-Ti-O Modeling

The random grain model was next applied to sulfidation of Zn-Ti-O solids. From analysis of SEM micrographs, such as Figure 4.15a, Zn-Ti-O solids are typically comprised of variable size-grains. For the modeling, the solid structure was simplified by considering only two discrete grain sizes (discrete bimodal distribution). The sizes of these grains were estimated from the SEM micrographs of the unreacted sorbents. The relative mass fraction of each type of grains was calculated using the surface area and porosity of the solid. The modeling of sorbents Z2T-a and Z2T3 will be discussed. Modeling of the other types of Zn-Ti-O sorbents used a similar approach.

Sorbent Z2T-a consisted of two types of grains, namely small, spherical grains of approximately 0.05 μm radius, and flat, plate-like grains, of 0.2 μm (half-thickness). An estimate of the relative mass percentage of the two grains types finds approximately a 50-50 distribution from SEM micrographs and porosity and surface area measurements. For the modeling, it was assumed that there was no interaction between the two types of grains (i.e. no overlapping of products originating from the two different grain types).

For the spherical grains, similar reaction and structural equations were used as those for the modeling of ZnO (Section 5.4.1). For reactions of plate-like grains, Eq. 5.29-5.31 become

$$\epsilon_o = \exp [- 2A_{avg} r_o n_o] \quad (5.33)$$

$$S_o = n_o 2A_{avg} \epsilon_o \quad (5.34)$$

$$r_o = - \frac{\epsilon_o}{S_o} \ln \epsilon_o \quad (5.35)$$

The inclusion of a discrete bimodal distribution of grain size produced a good agreement between the experimental reaction profiles and the calculated profiles as can be seen in Figures 5.16 and 5.17. This agreement is much better than for the grain model (Fig. 5.7 and 5.8). Figure 5.16 shows the reaction profiles at 500°C for the spherical grains and plate-shaped grains. The individual contributions of these two types of grains to the overall conversion profile are also shown in Figure 5.16. The overall predicted conversion profiles at various temperatures are shown in Figure 5.17. The parameter values used to calculate the profiles in Figures 5.16 and 5.17 are listed in Table 5.4. Another improvement obtained by using the random grain model with a discrete bimodal grain size distribution for modeling the sulfidation of sorbent Z2T-a was the agreement between the effective diffusion coefficient predicted from the conversion profiles of both Z2T-a and Z2T-b sorbents. Z2T-a and Z2T-b differed only in their grain morphology. At 400°C, the calculated effective diffusion coefficient for Z2T-a was $1.8 \times 10^{-10} \text{ cm}^2/\text{s}$ while for Z2T-b, a value of $2.5 \times 10^{-10} \text{ cm}^2/\text{s}$ was calculated. Similar improvement between the predicted and experimental reaction profiles was obtained for sorbent Z2T3 using a bimodal grain size distribution in the random grain model as shown in Figures 5.18 and 5.19. (Compare with Fig. 5.9.) The parameter values used to calculate the profiles in Figures 5.18 and 5.19 are listed in Table 5.5.

Figure 5.16 Comparison of the experimental sulfidation profile of sorbent Z2T-a at 500°C (2%H₂S-1%H₂-97%N₂) with calculated profile from the random grain model. (Contributions of spherical and plate-like grains are also shown)

Figure 5.17 Comparison of experimental sulfidation profiles of Z2T-a (2%H₂S-1%H₂-97%N₂) with profiles calculated from the random grain model with a discrete bimodal grain size distribution.

Table 5.4 Parameter values used to calculate Z2T conversion profiles in Figures 5.16 and 5.17

50 wt% sphere-50 wt% plate

ρ_s (density, mmol/cm ³)	21.8
k (rate constant, cm/s)	$0.40\exp\{9.3\text{kcal/mol}/RT\}$
Molar Gas Composition	2% H ₂ S-1% H ₂ -97% N ₂
Z	1.45
b	0.5
De (cm ² /s) - 400°C	1.5×10^{-10}
500°C	2.2×10^{-9}
600°C	1.3×10^{-8}
700°C	8.3×10^{-8}
<u>sphere</u>	
ϵ_o (porosity)	0.42
r_o (grain radius, cm)	5.0×10^{-6}
<u>plate</u>	
ϵ_o (porosity)	0.72
r_o (grain radius, cm)	2.0×10^{-5}

Figure 5.18 Comparison of the experimental sulfidation profile of sorbent Z2T3 at 500°C (2%H₂S-1%H₂-97%N₂) with calculated profile from the random grain model. (Contributions of spherical and plate-like grains are also shown)

Figure 5.19 Comparison of experimental sulfidation profiles of sorbent Z2T3 (2%H₂S-1%H₂-97%N₂) with calculated profiles from the random grain model with a discrete bimodal grain size distribution.

Table 5.5 Parameter values used to calculate Z2T3 conversion profiles in Figures 5.18 and 5.19.

50 wt% sphere-50 wt% plate

ρ_s (density, mmol/cm ³)	11.7
k (rate constant, cm/s)	$0.40\exp[9.3\text{kcal/mol}/RT]$
Molar Gas Composition	2% H ₂ S-1% H ₂ -97% N ₂
Z	1.22
b	0.5
De (cm ² /s) - 400°C	3.5×10^{-11}
500°C	4.2×10^{-10}
600°C	3.6×10^{-9}
<u>sphere</u>	
ϵ_o (porosity)	0.42
r_o (grain radius, cm)	9.3×10^{-6}
<u>plate</u>	
ϵ_o (porosity)	0.81
r_o (grain radius, cm)	2.0×10^{-5}

5.5 EFFECT OF TiO₂ ON THE PRODUCT LAYER DIFFUSION

The calculated effective diffusion coefficients using the random grain model for the sulfidation of Zn-Ti-O sorbents of various zinc and titanium contents indicated a dependence on the relative amount of titanium in the sorbents. As Figure 5.20 shows, increasing the relative amount of TiO₂ causes a corresponding decrease in the effective product layer diffusion coefficient calculated for sulfidation at 400°C reacting in 2 mol% H₂S-1 mol% H₂-97 mol% N₂. The decrease in D_e with the relative amount of TiO₂ was linear. The best line fit through the points in Figure 5.20 was

$$D_e \text{ [cm}^2\text{/s]} = 2.67 \times 10^{-10} - 3.68 \times 10^{-12} y \quad (5.36)$$

where y is the mol% TiO₂.

The diffusion coefficient can be represented by an Arrhenius expression

$$D_e = D_0 \exp(-E/RT) \quad (5.37)$$

Arrhenius plots of the diffusion coefficients calculated with the random grain model for the sulfidation of sorbents ZnO, Z2T, and Z2T3 are shown in Figure 5.21. Table 5.6 lists the calculated Arrhenius constants. The Arrhenius plots of the diffusion coefficients are shown for temperatures up to 600°C. At higher temperatures, values for the diffusion coefficient became less accurate as the relative resistance of the chemical reaction increased compared to the diffusional resistance. The activation energies for all sorbents were approximately the same (26.6 ± 0.5 kcal/mol). The major difference was in the pre-exponential factor. The similarity in activation energies suggested that the diffusion mechanisms involved in sulfidation of both ZnO and Zn-Ti-O materials were the same.

Figure 5.20 Effect of relative amount of TiO₂ in the sorbents on the effective product layer diffusion coefficient.

Figure 5.21 Arrhenius plots of the product layer diffusion coefficients for various sorbents. Calculated with the random grain model from experiments with 2% H_2S -1% H_2 -97% N_2 .

Table 5.6 Arrhenius Constants for the Product Layer Diffusion Coefficient (D_e).

$$D_e = D_o \exp[-E/RT]^1$$

<u>Sorbent</u>	<u>Temp. Range, (°C)</u>	<u>Arrhenius Constants</u>	
		D_o , cm ² /s	E, kcal/mol
ZnO	400-600	0.098	26.4
Z2T	400-600	0.053	26.3
Z2T3	400-600	0.019	27.0

¹ R is the ideal gas constant and T is the absolute temperature (K)

During sulfidation of ZnO, a product layer of ZnS was formed. Diffusion across this product layer must occur before further reaction can occur. For the Zn-Ti-O sorbents, the product layer consisted of ZnS and TiO₂. From the XRD analyses of the sulfided sorbents, a mixture of α -ZnS, β -ZnS, and TiO₂ (anatase) was formed in sulfided Z2T. In sorbent Z2T3, sulfidation produced the same solid phases but instead of anatase, the rutile phase of TiO₂ was formed. The similarity in activation energies of the product layer diffusion coefficients calculated for the sulfidation of ZnO and Zn-Ti-O sorbents led to the conclusion that for the Zn-Ti-O sorbents diffusion occurred preferentially through ZnS rather than TiO₂. Thus, diffusion through ZnS was faster than through TiO₂. No effect was, therefore, observed with different TiO₂ crystal structures.

The measured activation energy (26.6 ± 0.5 kcal/mol) for the product layer diffusion coefficient obtained for sulfidation of ZnO is slightly higher than the value reported (22.0 kcal/mol) by Ranade and Harrison (1980). However, the pre-exponential factors differed significantly. Ranade and Harrison reported a value of 4.9×10^{-4} cm²/s, while this study found a value of 0.098 cm²/s. For example, at 400°C, the D_e measured in this study was 6.5 times higher than the reported value. The reason for this difference is not clear. However, the solid Ranade and Harrison studied was only 94.5% pure. It is not known how the unspecified impurity may have affected the product layer diffusion.

A series of sulfidation experiments were undertaken next using single crystal ZnO (0001) (Atomergic Chemetals Corp.) as well as single crystal ZnO coated with a thin film of TiO₂ (designated as TiO₂/ZnO) to verify that diffusion through ZnS was faster than through TiO₂. Details of this task are given in Lew's Ph.D. thesis (1990). Significantly

slower diffusion through TiO_2 than through ZnO was verified; for example, at 600°C the value of the diffusion coefficient was 3×10^{-8} and $9 \times 10^{-10} \text{ cm}^2/\text{s}$, respectively, for ZnS and TiO_2/ZnO .

As shown in Fig. 5.22, unlike the case of sulfidation of TiO_2/ZnO single crystal where diffusion through TiO_2 and ZnS occurs in series, during sulfidation of the bulk Zn-Ti-O sorbents diffusion through the mixed TiO_2 and ZnS crystals can occur in parallel. Since diffusion through ZnS is much faster than through TiO_2 , for the Zn-Ti-O sorbents diffusion through the product layer occurs mainly through ZnS grains. Diffusion preferentially occurs through the fastest pathway. The role of TiO_2 is to decrease the cross-sectional area available for diffusion and increase the tortuosity of the diffusion pathway. Hence, both the similarity in activation energy of the diffusion coefficients for ZnO and Zn-Ti-O sulfidation as well as the lower pre-exponential factors for Zn-Ti-O can be explained.

The change in the diffusion coefficient can be mathematically expressed by adapting the equation for the "random pore" model proposed by Wakao and Smith (1962) for diffusion in a porous solid having a bimodal pore-size distribution separated into macropores (m) and micropores (μ):

$$De = \epsilon_m^2 De_m + \left[\frac{\epsilon_\mu^2 (1 + 3 \epsilon_m)}{(1 - \epsilon_m)} \right] De_\mu \quad (5.38)$$

where ϵ_m and ϵ_μ are the macroporosity and microporosity, respectively. D_m and D_μ are the diffusion coefficients. For this system, a similar expression as equation (5.38) is used with the porosities replaced by the volume fractions (v) of ZnS and TiO_2 :

a) TiO_2/ZnO Single Crystal

b) Zn-Ti-O bulk sorbent

Figure 5.22 Schematic representation of diffusion layer for partially sulfided
a) TiO_2/ZnO single crystal and b) Zn-Ti-O bulk sorbent

$$De_{ZnS+TiO_2} = v_{ZnS}^2 De_{ZnS} + \left[\frac{v_{TiO_2}^2 (1 + 3v_{ZnS})}{(1 - v_{ZnS})} \right] De_{TiO_2} \quad (5.39)$$

The diffusion flux in the product layer is the sum of that through ZnS, that through TiO₂, and that through ZnS and TiO₂ in series. For $De_{ZnS} \gg De_{TiO_2}$, this reduces to:

$$De_{ZnS+TiO_2} = v_{ZnS}^2 De_{ZnS} \quad (5.40)$$

This equation (5.40) was used to predict the product layer diffusion coefficient for various Zn-Ti oxides sulfided at 400°C. As shown in Figure 5.23, the agreement between the experimental and predicted values was good.

The diffusivity was calculated using the H₂S concentration gradient. However, the large value of the activation energy (26.6 kcal/mol) implies ionic diffusion through a solid nonporous product layer. For a pore diffusion mechanism by Knudsen or bulk diffusion, D_e should vary with T^n where n is between 1/2 and 3/2. This would give an apparent activation energy of at most 0.0023 kcal/mol.

In the absence of spectroscopic or other complementary data, it was not possible to unambiguously determine the rate-limiting diffusing species in ZnS. However, from the present work and evidence from previous literature reports, the rate-limiting diffusing species can be inferred. Literature values were obtained by measuring the diffusion of an ionic species through ZnO or ZnS. This is different from the calculation performed in this study. The apparent diffusion coefficient, in this study, was calculated in a reacting system. Because of the volume changes associated with the formation of ZnS from ZnO, the diffusion layer (ZnS) may be formed with many defects. There was, thus, a greater oppor-

Figure 5.23 Comparison of predicted and experimental product layer diffusion coefficients with various Zn-Ti-O sorbents sulfided at 400°C .

tunity for surface and boundary diffusion, both of which are much faster than lattice diffusion, because an atom moving from one site to another is not forced to squeeze between atoms on all sides. Consequently, it is possible to obtain much higher apparent diffusion coefficient and lower activation energy.

The possible rate-limiting diffusing species are Zn and O ions diffusing out to the gas phase and S and H ions diffusing into the unreacted core. In addition, there is the possibility of electron diffusion to maintain the charge balance. The diffusion rate of H⁺ has been experimentally found to be very fast in ZnO compared to Zn and O ions. At 600°C, the diffusion coefficient of hydrogen in ZnO is 1.7×10^{-7} cm²/s (Thomas and Lander, 1956). This is much higher than the diffusion coefficient of oxygen or zinc in ZnO. There are some ambiguities in the measurements of the latter, perhaps due to variation in the defect concentration because of non-identical pretreatment conditions and to grain boundary diffusion contribution. However, for zinc ions diffusion through ZnO, the highest value reported for D is 3.0×10^{-14} cm²/s at 600°C (Secco, 1960). An activation energy of 20 kcal/mol and a pre-exponential factor of 3×10^{-9} cm²/s were calculated. For oxygen ions diffusion through ZnO, the highest value reported for D is 2.6×10^{-19} cm²/s (Robin et al., 1973) at 600°C. The last two values of D were extrapolated from results obtained at higher temperatures, 940-1141°C for oxygen diffusion measurement and 905-940°C for zinc diffusion. Since ZnO crystallizes in the hexagonal system, similar to wurzite (α -ZnS), it is expected that the relative order of increasing D for zinc, oxygen, and hydrogen species are the same in α -ZnS. Only values for the diffusion of zinc in α -ZnS were found for temperatures in the range of 927-940°C. Extrapolating to 600°C, D is 5.2×10^{-13} cm²/s

(Secco, 1958). Also, the activation energy is 35 kcal/mol and the preexponential factor is 3×10^{-4} cm²/s. These values were obtained with wurzite. Values for sphalerite (β -ZnS) should be approximately the same because the diffusing zinc species experiences the same diffusion paths and interstitial dimensions as in the wurzite structure (Secco, 1958). Secco (1958) determined that the diffusion mechanism of zinc is via interstitials. From geometrical considerations, he calculated the size of the interstitial in ZnS to be larger than in ZnO. The higher value of the diffusion coefficient for zinc ions in ZnS is then due to the larger size of interstices in ZnS than in ZnO.

No values of the S anion diffusion coefficient are available, but it is expected to be smaller since the ionic radius of S²⁻ is 2.45 times larger than Zn²⁺ (Shannon and Prewitt, 1969). Based on these values for the diffusion of zinc and oxygen ions, hydrogen ions cannot be the rate determining species because of their relatively high mobility. Hydrogen ions will be rapidly combined with oxygen anions to form OH⁻ by

Thus, instead of O²⁻ diffusing out, OH⁻ diffuses out.

It would be expected that the presence of H₂ changes the concentration gradient of Zn ions by the reaction

Hydrogen ions will rapidly diffuse towards the reactant-product interface. An increase in Zn ions concentration at this interface due to reaction (5.42) will change the zinc ions concentration gradient. Since no observable effect on D_c was found with various amounts

of H_2 (Section 4), it can be concluded that Zn cations are not the diffusion limiting species.

Similar arguments can be made for OH^- anions. At the interface between the solid product and the reactant gas, OH^- ions are consumed by the reaction

The presence of H_2O in the gas will increase the amount of OH^- ions at the gas-solid interface. This will decrease the diffusion of OH^- out of the solid by decreasing the concentration gradient. The rate of OH^- ions leaving the solid is

$$N_{OH^-} = D_e(C_{OH^-,p} - C_{OH^-,s}) \quad (5.44)$$

where $C_{OH^-,p}$ and $C_{OH^-,s}$ are the concentration of OH^- ions at the gas-solid product and solid product-solid reactant interface, respectively. N_{OH^-} is the transfer rate of OH^- out of the solid. The measured D_e will decrease because a change in the concentration gradient due to the presence of H_2O is not included in the calculation. As discussed in Section 4, no noticeable change in the sulfidation profiles was observed when various amounts of H_2O were added to the gas. Consequently, OH^- ions are not the diffusion limiting species.

The most probable diffusion limiting species are S^{2-} ions. The calculation of D_e was based on a gaseous concentration gradient ($C_{H_2S,g} - C_{H_2S,s}$). Since S^{2-} ions are diffusing, an ionic concentration gradient must be used. As shown in Figure 5.15, when the H_2S concentration was varied, it was not necessary also to vary the product layer diffusion coefficient to fit the data. Based on this observation and since the initial sulfidation reaction rate is first order, the chemisorption of H_2S on the solid is a first order process with

$$C_{S^{2-},p} = K_{H_2S} C_{H_2S,o} \quad (5.45)$$

where K_{H_2S} is the adsorption equilibrium constant of H_2S , and $C_{H_2S,o}$ is the bulk H_2S concentration. Thus, the rate expression (5.25) becomes:

$$\frac{dr_r}{dt} = \frac{\frac{-bk K_{H_2S} C_{H_2S,o}}{P_s}}{1 + \frac{k}{D_e} S_r \int_{r_r}^{r_p} \frac{dr}{S_{r,p}}} \quad (5.46)$$

Due to the limited scope of this study, it was not possible to determine the value of K_{H_2S} . A value of $K_{H_2S} = 1$ was used in calculating the diffusion coefficients. Other experimental methods, such as a radiotracer technique, can be used to determine the sulfur ion concentration in the diffusion layer. Thus, comparison with the diffusion coefficient from other studies must keep in mind that differences in values can be attributed to the value used for the driving force of diffusion.

5.6 SUMMARY/CONCLUSIONS

1. The grain model was successful in predicting the sulfidation profiles of ZnO but not the sulfidation of Zn-Ti-O sorbents. The difference is believed to be due to non-uniformity in the grain size of Zn-Ti-O materials.
2. The grain model overpredicted the grain size measured from SEM micrographs of ZnO sorbents. This was caused by overlapping of the grains which reduced the actual surface area of the sorbent.
3. The random grain model which allowed for randomly overlapping grains, gave a better agreement between the observed and predicted grain size. This model more realistically

simulated the grain structure of both ZnO and Zn-Ti-O sorbents.

4. A discrete bimodal grain size distribution with the random grain model successfully predicted the sulfidation profiles of Zn-Ti-O sorbents.

5. Diffusion of S^{2-} , the most plausible rate-controlling diffusing ion, was faster through ZnS (more than an order of magnitude faster) than through TiO_2 . TiO_2 in the product layer reduced the cross-sectional area for diffusion and increased the tortuosity of the diffusion path. Thus, the product layer diffusion coefficient decreased as the TiO_2 content in the product layer increased.

6. Although a drawback of Zn-Ti-O sorbents over ZnO is their lower De , at high temperature and with high sorbent surface area, product layer diffusion is relatively fast compared to the intrinsic sulfidation kinetics. Figure 5.24 shows the regions where kinetics and product layer diffusion are important as a function of particle size and temperature for sorbent Z2T-a.

Figure 5.24 Map of regions where kinetic and product layer diffusion are rate limiting

6. CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

A comparative study of the kinetics of reduction and sulfidation of zinc titanate and zinc oxide solids was undertaken in this project to determine the potential benefits of using zinc titanates over zinc oxide for hot coal gas desulfurization. Structural effects of reductive sulfidation were also examined on both types of sorbents. To aid the analysis, the sorbents were prepared from organic precursors in macroporous granular form, thus, eliminating pore diffusion resistances. The TGA reactor was operated under conditions free of gas-film diffusion limitations. Hence, the measured reaction rates were controlled only by intrinsic sorbent kinetics and/or product layer diffusion.

Structurally, the addition of TiO_2 into ZnO was found to be beneficial since fresh Zn-Ti-O solids (with up to 50 mol% TiO_2) were characterized by higher surface area and pore volume than ZnO neat prepared under similar conditions. While more than one of the three distinct zinc titanate phases (Zn_2TiO_4 , ZnTiO_3 , $\text{Zn}_2\text{Ti}_3\text{O}_8$) could be stabilized in mixed Zn-Ti-O solids calcined at temperatures below 800°C , all zinc titanates had identical intrinsic kinetics in dry reduction and in dry or wet sulfidation. This simplified testing and data analysis.

Initial reduction rates were lower for zinc titanates than ZnO neat. In dry reduction, addition of 25 mol% TiO_2 into ZnO is equally effective in suppressing the reduction rate (e.g. tenfold at 700°C) as higher TiO_2 contents. Wet reduction is slower for both ZnO and Zn-Ti-O materials. In this case, the initial reduction rate continues to decrease as the TiO_2 -content of the sorbent is increased. Reduction tests of partially sulfided ZnO and Zn-Ti-O

solids, indicated that H_2S inhibited the initial reduction rates similar to H_2O . Modeling reduction according to the data collected in this work, we have proposed poisoning of ZnO-reduction sites by titanium and developed rate expressions both in the presence and absence of water vapor. Further, we have explained the observed poisoning by a geometric effect of titanium oxide on ZnO-reduction sites. In contrast to the case of zinc ferrite, ZnFe_2O_4 , which breaks up into ZnO and Fe_3O_4 (or lower valence iron oxides) in a hot coal gas atmosphere, providing no stabilization to ZnO against reduction, the present study of the zinc titanates, has not identified any free ZnO in partially reduced Zn-Ti-O materials. Perhaps the ability of titanium to remain intimately associated with ZnO and, thus, possibly the reactive sites, in a reducing gas atmosphere can explain why Zn-Ti-O solids have lower reduction rates than Zn-Fe-O solids. Clearly, however, more information on the effect of various oxides on the reduction stability of ZnO is needed to elucidate the interaction mechanism.

The presence of titanium in ZnO was found to inhibit sintering of ZnS. In fact, Zn-Ti-O sorbents showed a measurable 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. 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 $\text{H}_2\text{S(g)}$ to form fine particles of ZnS(s) . Such structural effects were largely absent from the surface of Z2T-a

particles after reaction at the same conditions as ZnO.

No effect of water vapor on the sulfidation kinetics was observed for temperatures in the range of 400-700°C. However, the presence of H₂O enhanced the sintering of both ZnO and Zn-Ti-O sorbents undergoing sulfidation.

Zn-Ti-O sorbents allow raising the operating temperature for fuel gas desulfurization as a result of their lower reduction rate. For example, a solid with $(\text{Zn/Ti})_{\text{atomic}} = 2/3$ can operate at a sulfidation temperature 94 degrees Celsius higher than ZnO. This higher operating temperature compensates for the decrease in the sulfidation rate of ZnO upon addition of TiO₂.

At high sulfidation conversions, increasing the relative concentration of TiO₂ in the Zn-Ti-O solids led to lower rates of reaction due to a corresponding drop in the product layer diffusion coefficient. Because diffusion in TiO₂ was at least ten times slower than in ZnS, the product layer diffusion in zinc titanates was dominated by diffusion through ZnS. Consequently, similar activation energies for the product layer diffusion coefficient were obtained for the sulfidation of ZnO and Zn-Ti-O sorbents. TiO₂ merely served to decrease the cross-sectional area for diffusion and increase the tortuosity. Hence, the lower sulfidation rates at high TiO₂-contents. This effect is less significant at higher temperatures (> 650°C), where kinetics control the reaction rate.

6.2 RECOMMENDATIONS

In practice, most coal gas streams are quenched at the gasifier exit and, thus, contain significant amounts of water vapor (10-50 mol%). When water vapor is present, the reduction of ZnO is suppressed to the extent that only when the relative concentration of

titanium is increased substantially is there also a further substantial decrease in the reduction rate. The recommended sorbent composition depends on the tolerable level of sorbent loss due to reduction and the desired sulfur loading. As an example, the wet reduction rate of sorbent Z3T (3 Zn : 1 Ti) at 700°C is only half that of ZnO, while sorbent Z2T3 (2 Zn : 3 Ti) has a reduction rate nearly 9 times slower than ZnO, and an initial sulfidation rate of only half that of ZnO. However, the sulfur loading of Z2T3 is only 0.15 g sulfur/g sorbent (based on complete sulfidation), and its product layer diffusion coefficient in sulfidation is *ca.* 7 times slower than ZnO. However, for Z2T3 with a typical surface area of 2 m²/g, the overall rate is controlled by product layer diffusion only when the temperature is below 520°C. Between 520-1020°C, both chemical kinetics and product layer diffusion control the overall sulfidation rate.

The important structural differences between zinc titanate and zinc oxide sorbents discovered in this work provide the major motivation for the use of zinc titanates both in fixed - or fluidized - bed sorber configurations. Structural advantages may offset the kinetic and low-capacity drawbacks of TiO₂-containing ZnO for practical application to hot coal-gas desulfurization. Additional fundamental work on the structural stability of this type of sorbents and ways to promote it are needed to guide further development of the Zn-Ti-O materials. Further studies of cyclic sulfidation/regeneration of Zn-Ti oxides are also needed to establish whether the regeneration chemistry and kinetics, structural stability and performance regenerability of these sorbents justifies their selection over other competing systems as fully regenerable, attrition-resistant, high-temperature sulfur sorbents, suitable for commercial applications.

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