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Registry No. Dimethylol-4,5-DMOEU, 4211-44-3; 4,5-DMOEU, 3891-44-9; DMDHEU, 1854-26-8; 1,3-dimethyl-4,5-DHEU, 3923-79-3; 4,5-DHEU, 3720-97-6; DMDHEU (tetramethyl ether), 4356-60-9; HCHO, 50-00-0.

Literature Cited

- American Association of Textile Chemists and Colorists AATCC *Technical Manual*; AATCC: New York, 1987; Vol. 62.
- Andrews, B. A. Kottes Use of Reversed-Phase High-Performance Liquid Chromatography in Characterizations of Reactants in Durable-Press Finishing of Cotton Fabrics. *J. Chromatogr.* **1984**, *228*, 101-110.
- Andrews, B. A. Kottes An Update on Testing for Formaldehyde Release. *Textile Chem. Color.* **1987**, *19*, 19-26.
- Andrews, B. A. Kottes; Reinhardt, R. M. Process to Produce Durable Press Low Formaldehyde Release Cellulosic Textiles. US Patent 4,488,878, Dec 18, 1984.
- Andrews, B. A. Kottes; Reinhardt, R. M. Agents to Produce Durable Press Low Formaldehyde Release Cellulosic Textiles: Etherified *N,N*-Bis(Hydroxymethyl) Carbamates. US Patent 4,539,008, Sept 3, 1985.
- Andrews, B. A. Kottes; Reinhardt, Robert M. Assessment of Steady-State Free Formaldehyde in Durable Press Cotton Fabrics. *Text. Res. J.* **1986**, *56*, 115-120.
- Andrews, B. A. Kottes; Reinhardt, Robert M. Reaction Equilibria and Textile Performance from Low Formaldehyde Release Carbamate Finishing. *Text. Res. J.* **1989**, *59*, 53-60.
- Andrews, B. A. Kottes; Reinhardt, Robert M.; Trask-Morrell, B. J. Influence of Prolonged Storage on Formaldehyde Liberation from Durable Press Textiles. *Text. Res. J.* **1988**, *58*, 255-263.
- Andrews, B. A. Kottes; Harper, Robert J., Jr.; Vail, S. L. Variables That Influence Formaldehyde Release from Cottons Finished for Durable Press. *Text. Res. J.* **1980a**, *50*, 315-321.
- Andrews, B. A. Kottes; Harper, Robert J., Jr.; Smith, Richard D.; Reed, John W. Lowering Formaldehyde Release with Polyols. *Text. Chem. Color.* **1980b**, *12*(11), 25-29.
- Beck, Keith, et al. GC/MS Analysis of Durable Press Agents. *Text. Chem. Color.* **1988**, *20*(3), 35-39.
- Harper, R. J., Jr.; Andrews, B. A. K.; Harris, J. A.; Reinhardt, R. M.; Vail, S. L.; Bathija, A. P.; Ulsamer, A. G. Formaldehyde Release from Labeled and Unlabeled Cross-linked Cotton and Cotton-Polyester Fabrics. Agricultural Research Service, Agricultural Research Results, ARR-S-17/May 1984.
- Lange, N. A. *Handbook of Chemistry*, 10th ed.; McGraw-Hill: New York, 1961; p 952.
- North, Bernard F. New Ultra-Low H₂CO Resins. *Am. Dyestuff Repr.* **1983a**, *72*(5), 32-35.
- North, Bernard F. Treating Cellulose Textile Fabrics with Dimethylol Dihydroxyethyleneurea-Polyol. US Patent 4,396,391, Aug 2, 1983b.
- Pasad, Dilip; Beck, Keith Quantitative Analysis of Commercial Durable-Press Finishes by HPLC. *Text. Chem. Color.* **1986**, *18*(5), 27-32.
- Reinhardt, Robert M. Vapor Transport of Formaldehyde to Cotton. *Text. Res. J.* **1983**, *53*, 175-180.
- Reinhardt, Robert M.; Andrews, B. A. Kottes *Ind. Eng. Chem. Res.* **1988**, *27*(3), 35-39.

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High-Temperature H₂S Removal from Fuel Gases by Regenerable Zinc Oxide-Titanium Dioxide Sorbents

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Bulk Zn-Ti-O binary oxides and ZnO were synthesized in macroporous and dispersed form by the amorphous citrate technique. The addition of TiO₂ into ZnO stabilized ZnO against reduction to volatile elemental zinc at 650 °C in a simulated coal gas mixture of 1% H₂S-13% H₂-19% H₂O-67% N₂. The intrinsic sulfidation kinetics of zinc titanates were similar to zinc oxide at 650 °C. Cyclic sulfidation-regeneration experiments were performed in a packed-bed microreactor. The H₂S removal efficiency of Zn-Ti-O materials was as high as that of ZnO removing H₂S to less than 1-5 ppm until breakthrough. Although zinc titanates typically had low sulfidation conversion (50-60%), this problem could be eliminated by preparing the sorbents from a chloride precursor.

High-temperature desulfurization of coal-derived fuel gas offers improvements on the thermal efficiency of emerging technologies using coal gasification such as integrated gasification combined-cycle power generation employing gas turbines, and gasifier-molten carbonate fuel cell power plants. For these technologies, highly efficient sulfur removal from several thousand parts per million (ppm) down to ~1 ppm for fuel cell power plants or ~100 ppm for gas turbines is needed. Commercial desulfurization processes are based on liquid scrubbing at or below ambient temperatures, resulting in considerable thermal efficiency loss as well as costly wastewater treatment.

Early work on hot gas desulfurization employed single oxide sorbents, especially iron oxide and zinc oxide

(MERC, 1978; Grindley and Steinfeld, 1981). From the standpoint of high H₂S removal efficiency, zinc oxide is more attractive than iron oxide because of more favorable sulfidation thermodynamics. However, the sulfidation kinetics of ZnO are much slower than those of iron oxide. The regenerability of ZnO is restricted by loss of surface area (sintering) at high regeneration temperatures and formation of zinc sulfate at low regeneration temperatures. Also, during sulfidation, reduction of ZnO followed by vaporization of elemental zinc can take place at temperatures as low as 600 °C.

Recently, the two oxides of iron and zinc were combined into the mixed oxide (spinel) compound zinc ferrite, ZnFe₂O₄, which has been found to possess H₂S removal efficiency comparable to ZnO but somewhat better capacity (Grindley and Steinfeld, 1981). However, the drawbacks of zinc ferrite are also similar to those outlined above for ZnO.

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Table I. Physical Properties of Fresh Sorbents^a

sorbent	atomic metal ratio (Zn:Ti)	calcination temp (°C), time (h)	pore volume, cm ³ /g	BET surface area, m ² /g	porosity, %	pore size distribution, %			
						>25 μm	25-1 μm	1-0.1 μm	0.01-0.003 μm
ZT	1:1	750, 5	1.5	20.0	89	50	25	7	18
ZT2-Cl ^b	0.43:1	700, 5	2.0	5.1	86	40	30	18	12
Z2T-Cl ^c	2:1	720, 12	1.5	4.6	89	15	66	14	5
Z2T	2:1	700, 12	0.75	4.1	93	55	27	9	9
Z2T3	2:3	700, 12	0.29	1.3	60	45	25	13	17
ZnO(550)		550, 4	3.0	7.2	94	55	21	11	13
ZnO(720)		720, 4	1.2	2.4	87	15	62	21	2

^a-20 to +35 mesh granules, except for Z2T-Cl and ZnO(720), which were -115 to +170 mesh granules. ^bPrepared from TiCl₄ and zinc acetate. ^cPrepared from ZnCl₂ and titanium(IV) isopropoxide.

Table II. Crystalline Phases and Physical Properties of Various Zn-Ti-O Sorbents

sorbent	crystalline phases (wt %) ^a	BET surface	
		area, m ² /g	pore ^b vol, cm ³ /g
ZT fresh	ZnO (11), ZnTiO ₃ (57), Zn ₂ Ti ₃ O ₈ (26), TiO ₂ (6)	20.0	1.50
ZT, 650 °C, sulfided, 11 cycles	β-ZnS (32), ZnTiO ₃ (27), TiO ₂ (23), unknown (18)	2.4	0.80
ZT, 700 °C regenerated, 11 cycles	ZnTiO ₃ (88), Zn ₂ TiO ₄ (9), TiO ₂ (3)	3.6	0.81
ZT2-Cl, fresh	ZnTiO ₃ (69), TiO ₂ (31)	5.1	2.0
ZT2-Cl, 650 °C sulfided, 6 cycles	α-ZnS (27), ZnTiO ₃ (15), TiO ₂ (58)	2.9	1.3
ZT2-Cl, 700 °C regenerated, 6 cycles	ZnTiO ₃ (56), Zn ₂ TiO ₄ (11), TiO ₂ (33)	2.5	1.5
Z2T3, fresh	ZnTiO ₃ (83), TiO ₂ (17)	1.3	0.29
Z2T, fresh	ZnO (4), Zn ₂ TiO ₄ (96)	4.1	0.75
Z2T, 650 °C sulfided, 5 cycles	Zn ₂ TiO ₄ (3), α-ZnS (50), Zn ₂ Ti ₃ O ₈ (25), unknown (22)	2.0	NM ^c
Z2T, 700 °C regenerated, 5 cycles	ZnO (8), Zn ₂ TiO ₄ (92)	1.9	0.80
Z2T-Cl, fresh	Zn ₂ TiO ₄ (100)	4.6	1.5 ^d

^aIdentified by XRD. ^b-20 to +35 mesh granules. ^cNM = not measured. ^d-115 to +170 mesh granules.

This work has focused on the potential use of ZnO-TiO₂ mixtures as high-temperature, regenerable H₂S sorbents. A related previous study of zinc titanate materials for hydrodesulfurization (HDS) of fluid streams can be found in a patent by Farha and Gardner (1982). In that work, zinc orthotitanate, Zn₂TiO₄, promoted with various metals was used as a HDS catalyst and in partially sulfided form was used for absorption of H₂S at low temperatures (205-538 °C). Regeneration of the sulfided sorbent with air was also reported in that patent. In our study, TiO₂ was selected as an additive to ZnO to potentially stabilize ZnO against undesired reduction without considerably compromising the good sulfidation equilibria of pure ZnO. Lercher and others (1984) have reported that the amount of Zn²⁺ cations on the surface of ZnO-TiO₂ mixtures decreases as the content of TiO₂ increases, thus raising the possibility of stabilizing ZnO against reduction by addition of TiO₂.

On the basis of available thermodynamic values (Barin and Knacke, 1973; Barin et al., 1976), zinc orthotitanate has sulfidation equilibria inferior to ZnO (or ZnFe₂O₄, which breaks down into ZnO + Fe₃O₄ in the presence of hydrogen or carbon monoxide). However, zinc orthotitanate has higher sulfidation equilibrium constants than other zinc compounds, such as aluminates or silicates.

The ZnO-TiO₂ system has been of interest in the titanium dioxide pigment industry. Cole and Nelson (1938) reported the formation of oxide solid solutions in this system, although this was not observed by other investigators (Dulin and Rase, 1960; Bartram and Slepetyts, 1961; Reddy et al., 1984). The most commonly found compounds in this system are zinc orthotitanate (Zn₂TiO₄), zinc metatitanate (ZnTiO₃), and Zn₂Ti₃O₈.

In this paper, we report on fuel gas desulfurization by several ZnO-TiO₂ mixtures as well as ZnO neat sorbents prepared by a special technique as highly porous materials. The reduction stability of these sorbents was examined in various gas mixtures. The sorbent performance in successive sulfidation-regeneration cycles is discussed in terms

of sorbent composition and pore structure.

Experimental Section

Preparation and Characterization of Sorbents.

Bulk sorbents were prepared by a complexation method for synthesizing highly dispersed mixed oxides from amorphous citrate precursors (Courty et al., 1973). This method consists of dehydration first rapidly (~15 min) in a rotary evaporator under vacuum and then slowly (3-24 h) in a vacuum oven at 70 °C of an aqueous solution of zinc acetate or zinc chloride, titanium(IV) isopropoxide, or titanium tetrachloride and citric acid to form a highly porous solid foam. An equal mole ratio of citric acid to metal ions is typically used in preparation of the solution. The solid foam is calcined in air in a muffle furnace at 550-850 °C for 4-8 h, producing a porous, homogeneous mixed metal oxide.

The fresh, sulfided, and regenerated sorbents were characterized by several bulk and surface analysis techniques. X-ray diffraction (XRD) for identification of crystalline phases in the mixed oxide sorbents was performed in a Siemens Allis D500 instrument using a Cu Kα source. Scanning electron microscopy (SEM) combined with energy dispersive X-ray analysis (EDX) using a Cambridge Stereoscan 250 MK3 instrument was used to observe the surface morphology, crystallite size, and spatial variation of elemental distribution of the sorbents. Surface areas were measured by a Micromeritics Flow Sorb II 2300 BET apparatus using N₂ gas. Pore volume and pore size distribution of the sorbents were obtained with a Micromeritics Autopore 9200 mercury porosimeter. Porosity measurements were performed by He pycnometry coupled with Hg porosimetry. Atomic absorption (AA) spectroscopy was used for elemental analyses.

Properties of Fresh Sorbents. Table I lists the physical characteristics of fresh ZnO-TiO₂ and ZnO sorbents that were prepared and tested in this work. Two ZnO sorbents were prepared: ZnO(550) and ZnO(720), calcined at 550 and 720 °C, accordingly. The crystalline

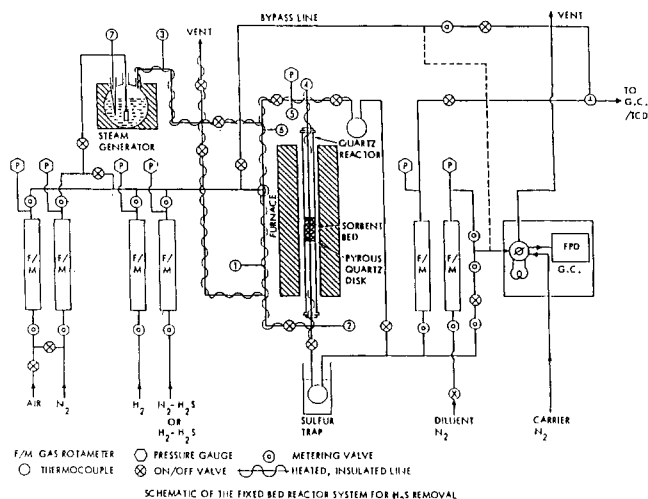


Figure 1. Schematic diagram of the packed-bed microreactor system used for sulfidation and regeneration studies.

phases identified by XRD in the mixed oxide sorbents are shown in Table II. The preparation and the physical properties of the sorbents are described in detail by Lew (1987).

Sorbents Z2T3 and Z2T, with a Zn/Ti ratio equal to 0.67 and 2.0, respectively, were prepared under similar calcination conditions (700 °C for 12 h). Under these conditions, higher TiO₂ content leads to lower pore volume and surface area. For sorbent Z2T3, the major crystalline phases identified by XRD were ZnTiO₃ and TiO₂. When the atomic ratio of Zn:Ti was 2:1, as in the case of sorbent Z2T, Zn₂TiO₄ was the only Zn-Ti-O compound present.

Relatively high pore volume material can be produced by increasing the amount of citric acid used in the preparation. Sorbent ZT prepared with twice the usual amount of citric acid had a pore volume of 1.5 cm³/g, which is much higher than either Z2T (0.75 cm³/g) or Z2T3 (0.29 cm³/g).

Using TiCl₄ as the TiO₂ precursor produced ZnO-TiO₂ sorbents (e.g., ZT2-Cl) with larger pore volume (~1.5 cm³/g) than those prepared from titanium(IV) isopropoxide even though the usual 1:1 citric acid to metals ratio was used in the preparation. The higher pore volume is attributed to loss of a volatile compound of zinc, possibly ZnCl₂, during calcination, based on the observation of white deposits on the furnace wall. Analysis (by AA and XRD) of the calcined Zn-Ti-O material confirmed the loss of zinc. Sorbent Z2T-Cl was prepared from another chloride precursor, zinc chloride, rather than TiCl₄. Titanium(IV) isopropoxide was used in the preparation of Z2T-Cl because of the greater difficulty in handling TiCl₄.

Apparatus and Procedure. The majority of the sulfidation-regeneration experiments were performed in a packed-bed microreactor system, schematically shown in Figure 1. The reactor consisted of a quartz tube, 1.5-cm i.d., which was mounted vertically inside an electric furnace equipped with a temperature controller. The axial bed temperature was measured with a chromel-alumel thermocouple inside a quartz thermowell (0.3-cm i.d.) concentric to the reactor. The sorbent bed, approximately 4–6 cm in height, consisted of -20 to +35 mesh particles supported on a fritted quartz disk. Gas mixtures were prepared by passing 2% H₂S-in-N₂, H₂ and N₂ in sulfidation experiments or air and N₂ in regeneration experiments from gas cylinders through purifiers (except for the H₂S/N₂ mixture) and flowmeters into a common gas line. The lines leading to the reactor were heated and insulated. Nitrogen bubbling through water maintained at constant

temperature in a three-necked flask assembly was used to introduce a known amount of water vapor into the feed gas mixture. The reactor pressure was maintained at slightly above atmospheric.

Sulfidation experiments were carried out isothermally at 600 and 650 °C with a gas mixture containing 13% H₂, 19% H₂O, 1% H₂S, and 67% N₂. This gas mixture simulated the typical exit gas from the air-blow KRW fluidized-bed coal gasifier with CO and CO₂ made up by N₂. The sulfided sorbents were regenerated in 10% air-90% N₂ at 700 °C. The gas hourly space velocity, SV, for both sulfidation and regeneration was ~2000 h⁻¹ (STP). After one or more sulfidation runs, deposits on the cool walls of the quartz tube were extracted and analyzed by AA for zinc.

The product gas was passed through ice traps to condense any elemental sulfur formed. The gas was analyzed for H₂S and SO₂ by a HP-5880A gas chromatograph equipped with both flame photometric (FPD) and thermal conductivity (TCD) detectors.

Kinetic experiments of sorbent reduction and sulfidation were carried out in a Cahn 113-X thermogravimetric analyzer (TGA) equipped with a Cahn 2000 electrobalance, a Micricon temperature controller, and a Bascom Turner data acquisition system. The balance section of the TGA was constantly purged with nitrogen gas flowing at a known flow rate. The reactant gas was introduced into the apparatus through a side stream. Gas flow rates were set by mass flow controllers. The particle size of the reactant solid was between -115 and +170 mesh. The solid sample was placed in a quartz pan which was suspended by a hangdown wire inside a vertical quartz tube heated by an electric furnace. Initially, a nichrome hangdown wire was used. However, the nichrome wire reacted with hydrogen sulfide. A quartz wire used in place of the nichrome wire eliminated this problem. The temperature of the sample was measured using a chromel-alumel thermocouple placed directly beneath the pan. When the temperature reached the desired value, the reactant gas was allowed into the reactor, and the sample weight was monitored as a function of time.

In the experiments performed in the TGA, the total flow rate and the amount of sample used were chosen such as to avoid external mass-transfer limitation. Small particle sizes were chosen to avoid diffusional limitations within the particle. The only resistances measured in these experiments were due to kinetic limitations and, possibly, product layer diffusion limitations.

Results and Discussion

Experiments in the Packed-Bed Microreactor. The sulfidation performance of ZnO and zinc titanate sorbents was investigated in the packed-bed microreactor in terms of H₂S breakthrough curves. The results are discussed in this section as a function of the sorbent physicochemical properties.

In a typical sulfidation experiment, the hydrogen sulfide concentration in the product gas slowly rises until a certain time, after which it rises rapidly to the inlet value. The time of this abrupt change of slope of the H₂S elution profile is called the breakthrough time. The results below are presented in terms of the mole fraction (in ppm) of H₂S in the product gas versus a normalized time t/t^* , where t^* is the theoretical breakthrough time required for complete sulfidation of the sorbent. The ratio t/t^* , thus, represents the fractional conversion (based on ZnS formation) of the sorbent. Each figure includes several breakthrough curves corresponding to successive sulfidation cycles denoted by C-1, C-2, etc. The regeneration

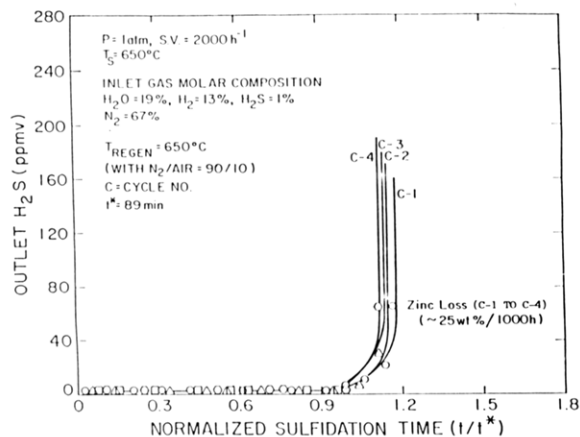
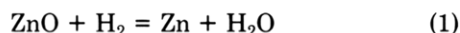


Figure 2. H₂S breakthrough curves in successive sulfidation cycles of sorbent ZnO(550).

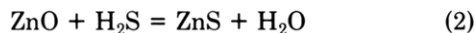
conditions between sulfidations are also listed. In the absence of transport and kinetic limitations, the H₂S elution profile or breakthrough curve would be a step function with $y = y^{eq}$ at $t < t^*$ and $y = y^o$ at $t > t^*$, where y^{eq} and y^o are the equilibrium and inlet mole fractions of hydrogen sulfide, respectively.

Zinc Oxide. Figure 2 shows successive sulfidation cycles each followed by regeneration with a 10 mol % air–90 mol % N₂ at 700 °C for the ZnO(550) sorbent. Complete sorbent conversion and subequilibrium (below 5 ppm) H₂S levels in the exit gas are seen in Figure 2. This is in agreement with previously reported data for ZnO sulfidation (Flytzani-Stephanopoulos et al., 1985; Tamhankar et al., 1986). Subequilibrium H₂S levels as well as conversion exceeding 100% may be explained by additional H₂S retention on the sorbent through the formation of a surface ZnS of different thermodynamics than bulk sulfide phases. This has been reported for the case of nickel sulfide (Rostrup-Nielsen, 1975).

Zinc deposits were observed on the wall of the reactor downstream of the bed, indicating loss of volatile zinc by reduction of the zinc oxide sorbent



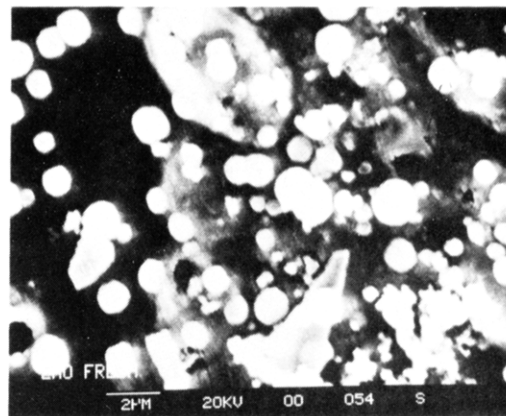
Reaction 1 occurs in addition to sulfidation of the sorbent



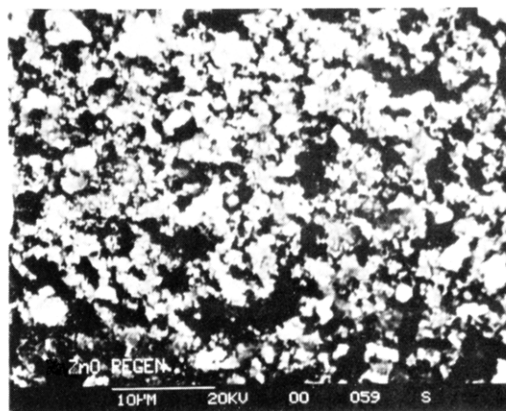
The zinc deposits were extracted in nitric acid and analyzed by AA. The average rate of zinc loss was found to be 25 wt % Zn/1000 h. Due to the short reaction times, the rate of zinc loss had negligible effects on the H₂S breakthrough curves of Figure 2. However, after many sulfidation–regeneration cycles, the continuing zinc loss will cause a noticeable decrease in the conversion of the sorbent to ZnS based on the original amount of ZnO.

Since a low oxygen concentration (2%) was used in regeneration of the sulfided sorbent, zinc sulfate formation was not observed. One interesting observation during ZnO regeneration was a higher surface area in the regenerated sorbent. The surface area of the regenerated sorbent was 11.9 m²/g after cycle 4, while the surface area of the fresh sorbent was only 7.2 m²/g. The SEM micrographs of the fresh and regenerated sorbent are shown in Figure 3. While the fresh sorbent consists of dispersed hexagonal crystals, the surface of the regenerated ZnO(550) is different, consisting of needlelike crystals due to oxygen-induced “surface roughening”.

Zinc Titanates. Figure 4 shows the stabilized sulfidation performance of bulk ZnO(550), Z2T, Z2T3, and ZT2-Cl sorbents at 650 °C. The crystalline phases and physical properties of several sulfided and regenerated



(a)



(b)

Figure 3. SEM micrographs. (a) Fresh ZnO(550) sorbent. (b) Regenerated ZnO(550) sorbent showing the surface roughening.

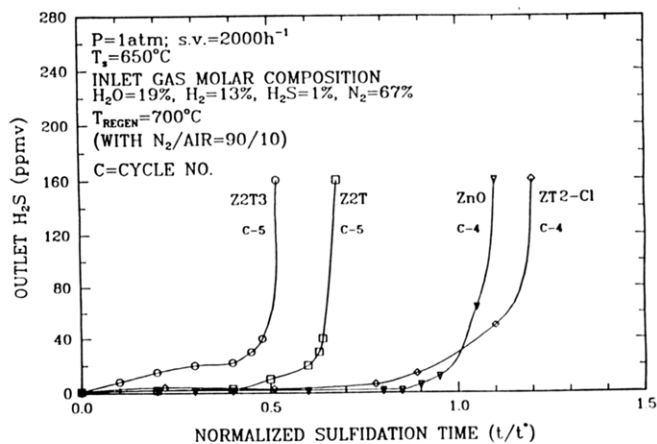
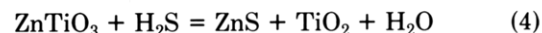
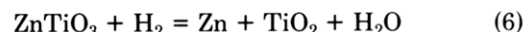
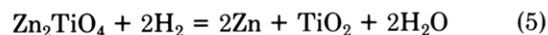


Figure 4. H₂S breakthrough curves for sorbents ZnO(550), Z2T (2Zn:1Ti), Z2T3 (2Zn:3Ti), and ZT2-Cl (0.4Zn:1Ti) after stabilized performance has been attained in sulfidation at 650 °C.

ZnO–TiO₂ sorbents are listed in Table II. The sulfidation reactions that may occur with the various zinc titanate phases present are



in addition to reduction reactions



Sorbent Z2T (2Zn:1Ti) consisting predominantly of Zn₂TiO₄ had H₂S removal efficiency similar to ZnO. However, this material reached only 65% conversion at break-

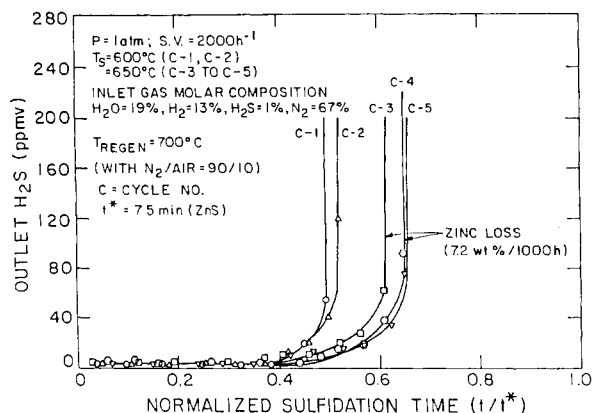


Figure 5. H₂S breakthrough curves in successive sulfidation cycles of sorbent Z2T.

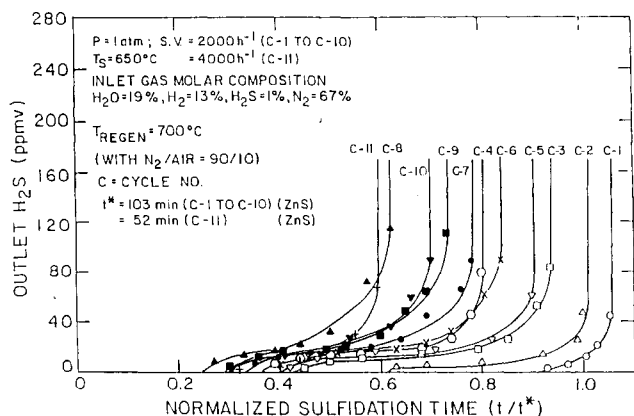


Figure 6. H₂S breakthrough curves in successive sulfidation cycles of sorbent ZT showing progressively poorer performance.

through. XRD analysis found unreacted Zn₂Ti₃O₈ in the sorbent. Even lower (50%) breakthrough conversion was observed with sorbent Z2T3 (2Zn:3Ti). There are several potential explanations for the lower conversion of zinc titanate sorbents. The intrinsic sulfidation kinetics of zinc titanate phases may be slower than for zinc oxide, pore plugging may be occurring due to the lower pore volume of the zinc titanate sorbents, or gas diffusion through a product layer of zinc sulfide and titanium dioxide may be much slower than diffusion through a zinc sulfide layer alone. Experiments performed in the TGA aimed at elucidating the lower overall conversion of zinc titanates are discussed in the following sections.

In general, Z2T and Z2T3 were very regenerable. Cyclic sulfidation-regeneration experiments were reproducible. The H₂S breakthrough curves for Z2T are shown in Figure 5. The amounts and types of crystalline phases in Z2T regenerated at the end of cycle 5 remained virtually the same as in the fresh sorbent (Table II). Even though during sulfidation two separate phases, ZnS and TiO₂, were formed, during regeneration Zn₂TiO₄ was again formed. This indicates the stability of zinc titanate phases.

The sorbent ZT (1Zn:1Ti) was prepared with high surface area (20 m²/g) and high pore volume (1.5 cm³/g) to study the role of these physical properties on the performance of the material. Figure 6 shows H₂S breakthrough curves for this sorbent. Full conversion was reached in the first cycle of operation. However, the sulfidation performance of this sorbent gradually deteriorated with succeeding cycles. After the final cycle, the pore volume and surface area (Table II) decreased substantially to 0.81 cm³/g and 3.6 m²/g, respectively. The pore volume of the sulfided sorbent was 0.80 cm³/g. Since both the sulfided and regenerated sorbent had approxi-

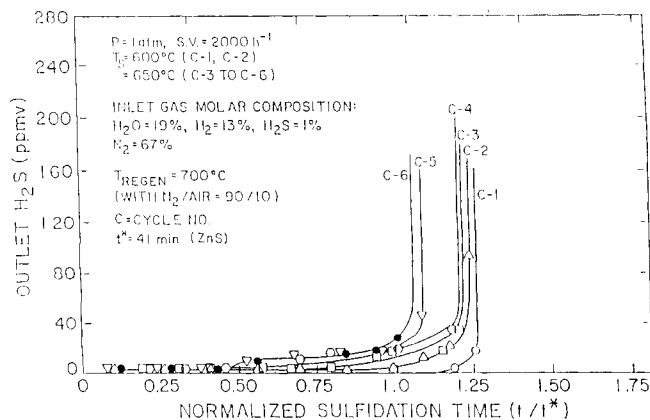


Figure 7. H₂S breakthrough curves in successive sulfidation cycles of sorbent ZT2-C1.

mately the same pore volume, it can be concluded that pore plugging is not the reason behind the poor performance.

Sorbent ZT2-C1 (0.4Zn:1Ti), unlike the other zinc titanates, had a high conversion even after several cycles. The sulfidation breakthrough curves for ZT2-C1 are shown in Figure 7. At 650 °C, the conversion of this sorbent varied from 100% to 135% (based on ZnS formation). The high sulfur capacity cannot be explained by absorption of H₂S by the TiO₂ component of the sorbent because sulfidation experiments with pure TiO₂ found the amount of H₂S absorbed to be negligible. However, sulfur incorporation into the Zn-Ti-O lattice takes place by some mechanism. To what extent residual chloride ions (present as an interstitial impurity) distort the ZnO-TiO₂ lattice, which in turn affects the sulfidation mechanism, is not presently known. ZnO-TiO₂ solid solutions that may be formed in the presence of interstitial impurities (Dulin and Rase, 1960) will have completely different sulfidation thermodynamics. However, wide-angle XRD analysis of ZT2-C1 did not identify any oxide solid solutions.

An explanation for the much higher conversion level of ZT2-C1 compared to other zinc titanate sorbents may be that the presence of chloride ions affects the rate of nucleation of products or the growth of the crystallites (Houte et al., 1981), in such a way that the product layer is much more dispersed. Thus, easy access to the reactant solid is maintained throughout the reaction.

The rate of zinc loss from zinc titanate sorbents during sulfidation in the reducing gas atmosphere was lower than for zinc oxide sorbents. At 650 °C, the average rates of zinc loss for Z2T and Z2T3 sorbents were 7 and 5 wt % Zn/1000 h, respectively. Average rates were computed from several successive sulfidation cycles. The average rate of zinc loss from ZT2-C1 was 8 wt % Zn/1000 h. By comparison, zinc loss from ZnO(550) was 25 wt % Zn/1000 h. Reduction and sulfidation experiments were also performed in the TGA apparatus in order to understand the lower propensity of zinc titanates to zinc losses as compared to zinc oxide. These are discussed in the next section.

Experiments in the TGA. Sorbent Sulfidation. Sulfidation experiments in the TGA were carried out with a high reactant gas flow rate (300–350 standard cm³) and small particle sizes (–115 to +170 mesh) to avoid external mass-transfer and internal diffusion resistances. The reaction profile will then reflect the intrinsic kinetics of the reaction, as well as diffusion through the product layer. Four different sorbents were studied in the TGA, namely, ZnO(720), Z2T, Z2T3, and Z2T-C1. The ZnO used for these experiments was calcined at 720 °C instead of 550 °C, and,

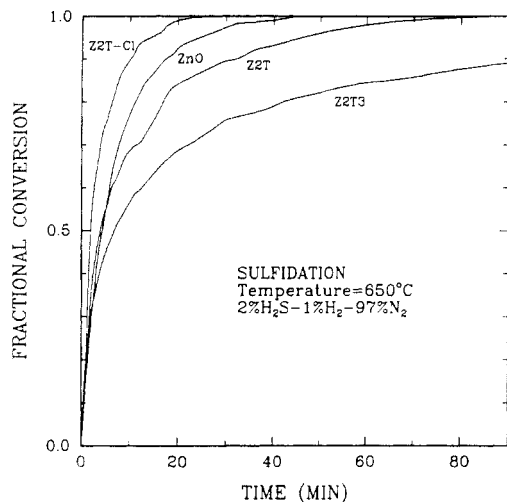


Figure 8. Sulfidation profiles of various sorbents measured in a TGA at 650 °C.

Table III. Rates of Reduction and Sulfidation of Bulk ZnO and Zn-Ti-O Sorbents at 650 °C^a

sorbent	BET surface area, m ² /g	initial reduction rate, ^b min ⁻¹	initial sulfidation rate, ^c min ⁻¹
ZnO(720)	2.4	1.9×10^{-2}	1.5×10^{-1}
Z2T	4.1	1.5×10^{-2}	2.1×10^{-1}
Z2T3	1.3	0.9×10^{-2}	2.0×10^{-1}
Z2T-Cl	4.6	1.5×10^{-2}	2.7×10^{-1}

^a Measured in the TGA apparatus using -115 to +170 mesh granules. ^b Reduction experiments performed with 10% H₂-90% N₂. ^c Sulfidation experiments performed with 2% H₂S-10% H₂-88% N₂.

therefore, had a lower surface area (2.4 m²/g). The last sorbent, Z2T-Cl, was prepared from a chloride precursor (ZnCl₂) and contained an atomic ratio of 2Zn:1Ti.

The reaction profiles for these sorbents are shown in Figure 8, in terms of fractional conversion versus time. The reaction was performed at 650 °C with 2% H₂S, 1% H₂, and 97% N₂. Measurement of the initial reaction rate provides information on the intrinsic sulfidation kinetics of each sorbent. At higher conversion, the rate of reaction is determined by a combination of the intrinsic kinetics and the diffusion through the product layer.

As shown in Figure 8 and Table III, the initial sulfidation rates for all zinc titanate sorbents are comparable to that of zinc oxide. Therefore, the limited conversion of zinc titanate sorbents observed in the microreactor experiments is not due to slower intrinsic sulfidation kinetics since both zinc oxide and zinc titanates have similar initial rates. The disparity in reaction rates occurs after significant conversion to ZnS and TiO₂ has occurred. From the reaction profiles of Figure 8, it can be concluded that limitation in the performance of zinc titanate sorbents is due to slow diffusion through a solid product layer. Higher content of titanium in the sorbent results in lower conversion as evident in the sulfidation of sorbent Z2T3 compared with that of Z2T (Figure 8).

A very different picture is seen in Figure 8 for the sulfidation profile of sorbent Z2T-Cl. The rate of reaction did not slow down as dramatically at later times as it did for the other zinc titanate sorbents (i.e., Z2T and Z2T3). In fact, the rate of sulfidation of Z2T-Cl at later times was higher than for ZnO. Apparently, diffusion through the product layer of sorbent Z2T-Cl proceeds at a faster rate. This agrees with the findings of Houte et al. (1981), who observed higher overall conversion in the sulfation of CaCO₃ when a chloride impurity was added. As previously

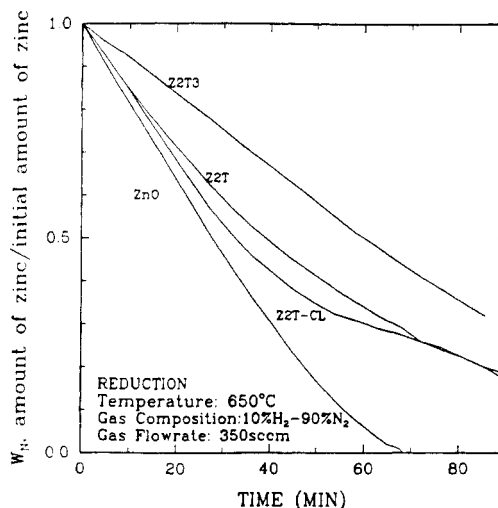


Figure 9. Reduction profiles of various sorbents measured in a TGA at 650 °C; W_N = amount of zinc at time (t)/initial amount of zinc.

mentioned, the authors attributed this to the formation of a dispersed product layer, facilitating sorbent diffusion.

Sorbent Reduction. The same four sorbents were exposed to a reducing gas mixture containing 10 mol % H₂-90 mol % N₂ at 650 °C. The reduction profiles for the fresh sorbents are shown in Figure 9 in terms of a normalized amount of zinc versus time. The rate of reduction was obtained through the measurement of the rate of zinc loss. The two rates are equivalent because the rate of reduction of ZnO to zinc metal is much slower than the rate of volatilization of the metal.

The experimental results in Figure 9 confirm that zinc titanate reduction rates are slower than zinc oxide reduction rates. Sorbent Z2T3 has the lowest rate of reduction of all the zinc titanate sorbents tested. There are two possible explanations for this observation. Either ZnTiO₃ present in Z2T3 is more resistive to reduction or TiO₂ also found in Z2T3 may surround the ZnTiO₃ phase, inhibiting the reaction. Table III lists the values of initial reduction rates for all sorbents examined. Sorbents Z2T and Z2T-Cl have approximately the same initial rates of reduction as ZnO, but at later times the reduction rates slow down noticeably. On the other hand, the rate of reduction of ZnO remains relatively unchanged throughout. For the zinc titanates, therefore, slower rates of reduction at high conversion are due to slow rates of diffusion through the TiO₂ product layer.

Another observation from Figure 9 is that the rate of reduction of Z2T is not as low in comparison with ZnO as expected from the previous experiments performed in the microreactor at 650 °C in 1% H₂S-13% H₂-19% H₂O-67% N₂. From those experiments, the rate of zinc loss was approximately 3.6 times lower for Z2T than for ZnO. It appears that the rate of reduction of the partially sulfided Z2T is slower than the fresh sorbent. To test this hypothesis, Z2T and ZnO were both partially sulfided to 10% conversion to ZnS. The partially sulfided sorbents were then reduced in 10% H₂-90% N₂ at 650 °C. Figure 10 shows the reduction profiles for these experiments. Also included, for comparison purposes, are the reduction profiles for the unreacted ZnO and Z2T. In Figure 10, complete reduction corresponds to loss of all the zinc present in the form of ZnO or zinc titanate. Zinc sulfide is not reduced. The rate of reduction of partially sulfided Z2T is much lower than for fresh Z2T in Figure 10. Such a drastic change in reduction rate is not seen for the partially sulfided ZnO. This further verifies the previous observation that the diffusion through the sulfided product

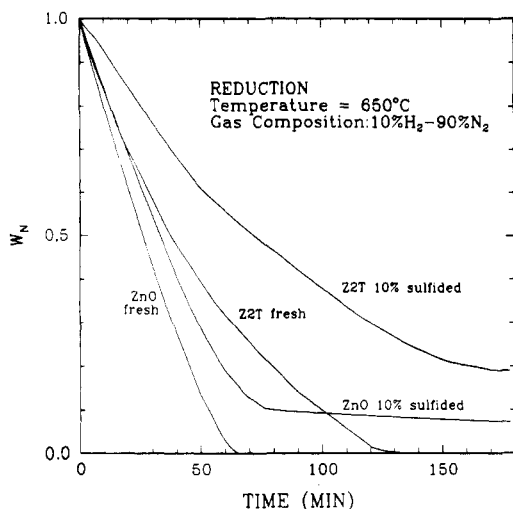


Figure 10. Comparison of the reduction profiles of partially sulfided (10%) ZnO(720) and Z2T with fresh ZnO(720) and Z2T; W_N = amount of zinc (as ZnO or ZnO-TiO₂) at time (t)/initial amount of zinc (as ZnO or ZnO-TiO₂).

layer of Z2T is much slower than that of ZnO. Furthermore, the sulfidation profiles of Z2T and ZnO (Figure 8) show that the two profiles do not begin to diverge until both have attained approximately 50% conversion. The sulfidation rate is not as adversely affected by the formation of the product as the reduction rate. A possible explanation of this may be that diffusion through the product layer of zinc vapor produced by reduction is much slower than the diffusion of the reactant gases.

Conclusions

Porous bulk binary oxides Zn-Ti-O and neat ZnO were synthesized from pyrolysis-calcination of amorphous citrate precursors. The main crystalline phase present in the sorbents with an atomic ratio of Zn:Ti ≤ 1 was ZnTiO₃. The Zn₂TiO₄ phase was formed for Zn:Ti = 2. These sorbents were tested both in sulfidation and reduction experiments in a packed-bed microreactor and a TGA apparatus.

This work has demonstrated enhanced overall performance of zinc oxide-titanium dioxide mixtures over neat zinc oxide for the desulfurization of coal-derived fuel gases. The major conclusions from the work presented in this paper are as follows: (1) Zinc titanates exhibit lower rates of zinc loss than zinc oxide during reduction-sulfidation of the sorbents at 650 °C in a simulated fuel gas atmosphere. (2) Zinc titanates have comparable intrinsic sulfidation kinetics to zinc oxides at 650 °C. (3) Zinc titanates have similarly high hydrogen sulfide removal efficiency as zinc oxides. (4) Sulfided zinc titanate sorbents are fully regenerable under the regeneration conditions employed in this work. (5) Incomplete sulfidation of zinc titanates is mainly due to slow diffusion through the product layer. (6) Zinc titanate sorbents prepared from chloride-containing precursors can be sulfided completely.

Zinc titanate sorbents represent an attractive alternative in high-temperature desulfurization processes where the high hydrogen sulfide removal efficiency of zinc oxide is desirable but where zinc loss represents a serious problem.

Future work will focus on elucidating the role that titanium dioxide plays in suppressing zinc loss and will attempt to optimize the composition and structure of Zn-Ti-O mixed oxide sorbents.

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Literature Cited

- Barin, I.; Knacke, O. *Thermochemical Properties of Inorganic Substances*; Springer Verlag: Berlin and New York, 1973.
- Barin, I.; Knacke, O.; Kubaschewski, O. *Thermochemical Properties of Inorganic Substances, Supplement*; Springer Verlag: Berlin and New York, 1976.
- Bartram, S. F.; Slepety, R. A. Compound Formation and Crystal Structure in the System ZnO-TiO₂. *J. Am. Ceram. Soc.* 1961, 44(1), 493-499.
- Cole, S. S.; Nelson, W. K. The System Zinc Oxide-Titanium Dioxide. Zinc Orthotitanate and Solid Solutions with Titanium Dioxide. *J. Phys. Chem.* 1938, 42, 245-251.
- Courty, P.; Ajet, H.; Marcilly, C.; Delmon, B. Oxydes Mixtes ou en Solution Solide sous Forme Tres Divisee Obtenus per Decomposition Thermique de Precurseurs Amorphes. *Powder Technol.* 1973, 7, 21-38.
- Dulin, F. H.; Rase, D. E. Phase Equilibria in the System ZnO-TiO₂. *J. Am. Ceram. Soc.* 1960, 43(1), 125-131.
- Farha, F. E., Jr.; Gardner, L. E. U.S. Patent 4,313,820, 1982.
- Flytzani-Stephanopoulos, M.; Gavalas, G. R.; Tamhankar, S. S.; Sharma, P. K. Novel Sorbents for High-Temperature Regenerative H₂S Removal. Final Report DOE/MC/20417-1898, 1985; METC, Morgantown, WV.
- Grindley, T.; Steinfeld, G. Development and Testing of Regenerable Hot Coal Gas Desulfurization Sorbents. Final Report DOE/MC/16545-1125, 1981; METC, Morgantown, WV.
- Houte, G. V.; Rodrique, L.; Genet, M.; Delmon, B. Kinetics of the Reaction of Calcium Sulfite and Calcium Carbonate with Sulfur Dioxide and Oxygen in the Presence of Calcium Chloride. *Environ. Sci. Technol.* 1981, 15(3), 327-332.
- Lercher, J. A.; Vinek, H.; Noller, H. TiO₂/ZnO Mixed Oxide Catalysts, Characterization by X-Ray Photoelectron and Infrared-Spectroscopy and Reactions with Propanol and Butanol. *Appl. Catal.* 1984, 12, 293-307.
- Lew, S. High-Temperature Regenerative H₂S Removal by ZnO-TiO₂ Systems. M.S. Thesis, Massachusetts Institute of Technology, Cambridge, 1987.
- MERC Hot Gas Cleanup Task Force Chemistry of Hot Gas Cleanup in Coal Gasification and Combustion. Final Report MERC/SP-72/2, 1978; MERC, Morgantown, WV.
- Rostrup-Nielsen, J. R. *Steam Reforming Catalysts*; Teknisk Forlag A/S; Copenhagen, Denmark, 1975.
- Reddy, V. B.; Goel, S. P.; Mehrotra, P. N. Investigations on Formation of Zinc Titanates Via Thermal Decomposition of Zinc Titanate Oxalate Hydrate. *Mater. Chem. Phys.* 1984, 10, 365-373.
- Tamhankar, S. S.; Bagajewicz, M.; Gavalas, G. R.; Sharma, P. K.; Flytzani-Stephanopoulos, M. Mixed-Oxide Sorbents for High-Temperature Removal of Hydrogen Sulfide. *Ind. Eng. Chem. Process Des. Dev.* 1986, 25, 429-437.

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