

THE REDUCTION OF ZINC TITANATE AND ZINC OXIDE SOLIDS

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Abstract—The reduction of bulk mixed oxides of zinc and titanium of various compositions and Zn–Ti–O crystalline phases was studied in a thermogravimetric apparatus in H₂–H₂O–N₂ gas mixtures at 550–1050°C. Comparative reduction experiments with ZnO were also performed. In the absence of water vapor, activation energies of 24 and 37 kcal mol⁻¹ were obtained for ZnO and Zn–Ti–O, respectively. The addition of water vapor inhibited reduction and resulted in a change in activation energy to 44 kcal mol⁻¹ for both ZnO and Zn–Ti–O solids. Similar to H₂O, H₂S inhibited the initial reduction rate of ZnO and Zn–Ti–O materials. Based on kinetic experiments, a two-site model is 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 H₂O, and is slowly eliminated by the presence of titanium.

INTRODUCTION

The efficient removal of H₂S from coal-derived gas streams at elevated temperatures is crucial for efficient and economic coal utilization in emerging advanced power generating systems such as the integrated gasification–combined cycle and the gasification–molten carbonate fuel cell. Typically, coal gases contain a mixture of CO, H₂, H₂O, CO₂, N₂ and CH₄. The composition of the gas mixture depends on the type of gasifier used and on the extent of the use of water for quenching. In addition to these gases, minor compounds, most of them undesirable or deleterious, such as H₂S and alkali salts, exit the coal gasifier. The relative amounts of these components depend on the type of coal and the type of gasifier used.

Previous studies (Jalan and Wu, 1980; Grindley and Steinfeld, 1981; Flytzani-Stephanopoulos *et al.*, 1985) have investigated zinc oxide as a high-temperature, regenerable sulfur sorbent. The thermodynamic equilibrium for ZnO sulfidation is quite favorable, yielding H₂S concentrations as low as a few parts per million (ppm) at typical hot gas cleanup temperatures (500–700°C). However, a difficulty with all sorbents containing zinc oxide is some reduction to volatile elemental zinc at temperatures above 600°C. ZnO reduction by H₂ has been detected at temperatures as low as 160°C (Bonasewicz *et al.*, 1981). The mixed oxide sorbent zinc ferrite, ZnFe₂O₄, combining ZnO with Fe₂O₃, has been developed in recent years as an alternative to single zinc oxide sorbent (Grindley and Steinfeld, 1983). Zinc ferrite decomposes into ZnO + Fe₃O₄ in the reducing coal gas atmosphere. Hence, it is similarly limited to an operating temperature of approximately 600°C. In recent studies (Lew *et al.*,

1989; Flytzani-Stephanopoulos *et al.*, 1987) the combination of zinc oxide with titanium dioxide was found effective in producing bulk mixed Zn–Ti–O as alternative, regenerable sulfur sorbents which may be more resistive towards reduction to volatile elemental zinc. This paper reports on kinetic and parametric studies of reduction of ZnO and Zn–Ti–O materials.

The reduction of ZnO in the temperature range of 400–1500°C by CO and H₂ gases 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. In more recent investigations (Truesdale and Waring, 1944; Hegedus and Kiss, 1966; Guger and Manning, 1971; Grunze and Hirschwald, 1974, 1975; Gioia *et al.*, 1977), the reduction kinetics of ZnO sintered pellets, powders, and single crystals were examined with H₂ as well as CO. Similar activation energies have been obtained for both reduction in H₂ and CO (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.

The first study of the reduction of Zn–Ti–O mixed oxides 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 reduction by hydrogen at 650°C. However, these experiments were carried out in a fixed-bed reactor, where mass transfer resistance might 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 a small amount of foreign atoms. They found that the reduction of ZnO can be inhibited by the addition of small amount (1 mol%) of Li₂O, Al₂O₃ or Ga₂O₃. They attributed this to a change in the electronic state of zinc oxide. However, no such information exists for the addition of TiO₂ into ZnO.

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The objective of this study 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 that suppresses reduction rate the most. The mechanisms and kinetics of the reduction of Zn–Ti–O solids were studied and compared with that of single ZnO to elucidate the role of titanium oxide in reduction. Only reduction by H₂ was investigated. From the studies of others (Grunze and Hirschwald, 1974), reduction of ZnO in H₂ is faster than in CO. Thus, the reduction rates obtained with H₂ represent the maximum amount of zinc loss possible in a coal gas atmosphere. In addition, the effect of H₂O on the rate of reduction was examined since H₂O is a major component in coal gases, and has been reported (Hegedus and Kiss, 1966; Flytzani-Stephanopoulos *et al.*, 1987) to inhibit the reduction of ZnO. The effect of H₂S on reduction was also investigated.

EXPERIMENTAL METHODS

Preparation and characterization of solids

Bulk mixed oxide solids of zinc and titanium were prepared by a known method for synthesizing highly dispersed mixed oxides from amorphous citrate precursors (Marcilly *et al.*, 1970; Courty *et al.*, 1973). The preparation of Zn–Ti oxides consists of slowly adding a 2:1 volume ratio solution of glacial acetic acid (Mallinckrodt, AR grade) and titanium(IV) isopropoxide (Strem Chemicals, AR grade) to an aqueous solution of zinc acetate (Mallinckrodt, AR grade) and citric acid monohydrate (Mallinckrodt, AR grade) under constant agitation. Typically, an equal mole ratio of citric acid to metal ions (zinc and titanium) is used in preparing the solution. The final solution is first dehydrated rapidly (15–30 min) in a rotary-vacuum evaporator at 65–75°C to form a viscous liquid and then dehydrated slowly (4–6 h) in a vacuum oven at 70–80°C to form a porous solid foam. The solid foam was calcined in air in a muffle furnace at 720°C for 12 h, producing a porous, homogeneous mixed metal oxide.

The solids were characterized by several bulk and surface analysis techniques. The elemental composition (zinc and titanium) of the solids was verified by atomic absorption spectroscopy (Perkin Elmer 360 Spectrophotometer) of the solids dissolved in a hot HF–HCl–H₂O solution (~90°C). X-ray diffraction (XRD) for identification of crystalline phases in the mixed oxides was performed with a Rigaku RU300 instrument using Cu(K α) radiation. Scanning electron microscopy (SEM) with a Cambridge Stereoscan 250 MK3 instrument was used to observe the surface morphology and crystallite size of the solids. Surface areas were measured by a Micromeritics Flow Sorb III 2300 BET apparatus using N₂ gas.

Apparatus and procedure

Kinetic reduction experiments with solids containing various Zn/Ti atomic ratios were performed in a

Cahn System 113-X thermogravimetric analyzer (TGA) equipped with a Cahn 2000 electrobalance, a Micricon temperature controller, and a Bascom–Turner data acquisition system. The TGA reactor system is shown in Fig. 1. The TGA measured the weight loss as a function of the time required for the reduction of Zn–Ti oxides to Zn and TiO₂, followed by rapid zinc vaporization. The chemical and physical properties of the solids used in reduction experiments are shown in Table 1. To ensure that the rate measurements were taken in the absence of gas phase diffusion limitation or equilibrium limitation, small amounts (1–2 mg) of material were used in each test and several samples were sintered at 1000°C for 1 h to minimize their surface area. In addition, the gas-flow rate was varied to ensure the absence of diffusional limitation.

Gas-flow rates were set by passing the H₂ and N₂ gases through Brooks Model 5850E mass-flow controllers. A gas flow rate of 485 cm³ min⁻¹ (STP) 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 or 51°C in a three-neck flask assembly. Calibration of the saturator was performed gravimetrically by measuring the weight change in a bed of Drierite placed downstream of the saturator. The saturated gas stream entered the apparatus side arm through heated lines. A thin layer of solid particles (~1 mg and 90–125 μ m size) was placed on a quartz pan suspended by a quartz hang-down wire. Isothermal reduction experiments were performed at temperatures between 550 and 1050°C. Each solid was pretreated in a vacuum oven at 90°C for 1 h to remove any absorbed H₂O before it was reacted in the TGA.

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% H₂S–1 mol% H₂–97 mol% N₂ and then reduced in 10 mol% H₂–90 mol% N₂.

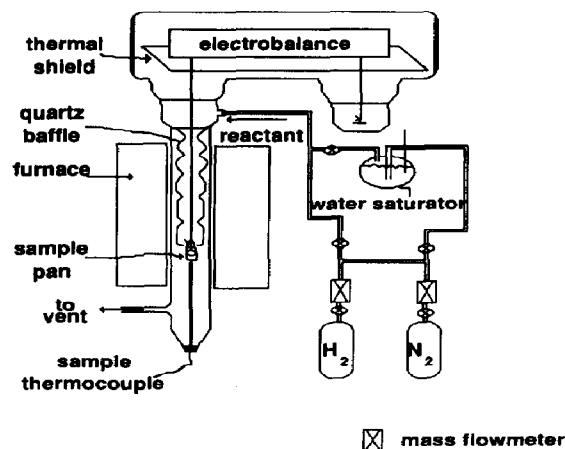


Fig. 1. Schematic of the thermobalance reactor system.

Table 1. Chemical and physical properties of solids used in reduction experiments[†]

Sorbent	Zn/Ti (atomic ratio)	Calcination temperature [‡] (°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 [§]	1.30	0	0	0	83	17

[†]Reduction experiments performed with 90–125 μm particles.

[‡]Sorbents calcined at 1000°C were first calcined at 720°C for 12 h.

[§]Calcined in the absence of air flow (static conditions).

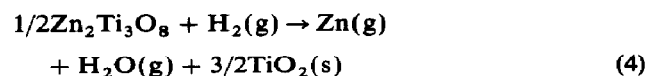
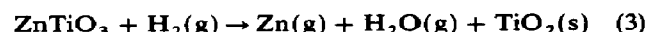
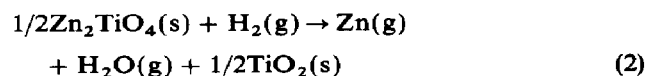
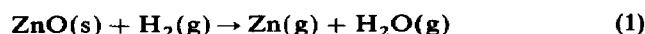
Sulfidation and reduction were performed at the same temperature.

$$R_0 = \frac{(dW/dt)_{t=0}}{(81.3794)A_0} \quad (6)$$

RESULTS AND DISCUSSION

Initial reduction rate of bulk Zn–Ti–O solids in 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 (i.e. ZnO, Zn₂TiO₄, ZnTiO₃ and Zn₂Ti₃O₈). Kinetic parameters were determined from these experiments. The possible overall reduction reactions are



To determine whether any reduction of TiO₂ occurs by reaction (5), both rutile (UCI 1090-113 extrusions crushed to 90–125 μm size particles) and anatase (obtained from Aldrich Chemical Co. in white powder form, 99.9% pure) were reacted with H₂ at 700–1000°C. The reduction of TiO₂ in hydrogen at elevated temperatures can be observed by a change in color from white to bluish gray (Matsuda and Kato, 1983) due to the formation of Ti₃O₅. No weight change of either crystalline form of TiO₂ was observed after 60 min in 10 mol% H₂–90 mol% N₂ at each temperature of 700, 800 or 1000°C. The color of TiO₂ changed to gray only after the experiment at 1000°C, indicating that surface reduction of TiO₂ took place under these conditions.

The initial reduction rate of various Zn–Ti–O materials listed in Table 1 was measured in 10 mol% H₂–90 mol% N₂. The initial rate was calculated by:

where the initial rate is R_0 (mmol cm⁻² s⁻¹), $(dW/dt)_{t=0}$ (mg s⁻¹) is the slope of the weight vs time profile at $t = 0$, 81.3794 is the molecular weight of ZnO, and A_0 (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 Fig. 2. 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 that of Zn–Ti–O solids with $(\text{Zn/Ti})_{\text{atomic}} \leq 3$ 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 (2Zn/1Ti) 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 the sorbents Z2T3-a (containing Zn₂Ti₃O₈, ZnTiO₃ and TiO₂) and Z2T3-b (containing ZnTiO₃ and TiO₂) gave similar initial reduction rates. This finding simplified the testing because it eliminated the need to prepare pure zinc titanate phases of the type Zn₂Ti₃O₈ or ZnTiO₃ 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 ZnO reduction, further kinetic experiments were performed. In the absence of both diffusional and external mass transfer resistances, an intrinsic initial heterogeneous rate expression of the form

$$R_0 = kC_{\text{H}_2}^n \quad (7)$$

was used, where k is the intrinsic rate constant, C_{H_2} is the molar concentration (mmol cm⁻³) of hydrogen

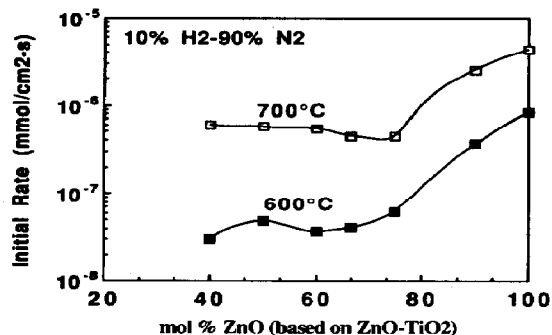


Fig. 2. Comparative plots of the initial reduction rate of various Zn-Ti-O materials reacted at 600 and 700°C in 10% H₂-90% N₂.

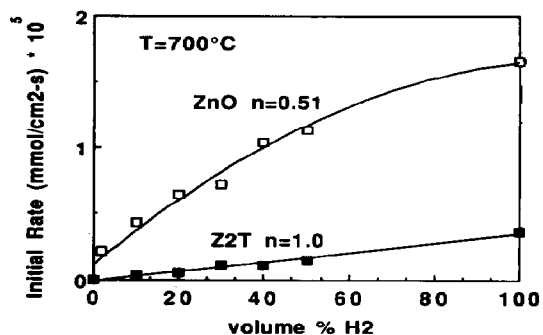


Fig. 3. Effect of hydrogen concentration on the initial reduction rate of ZnO and Z2T at 700°C.

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 Fig. 3. At 700°C, the reaction order obtained for ZnO was 0.51, while that of Z2T was one. The former result is in agreement with the work of Grunze and Hirschwald (1974, 1975) where fractional reaction orders for ZnO reduction were also observed. At 700°C and for pressure in the range of 1-4 torr, a reaction order of 0.60 was reported in that work.

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

$$k = k_0 \exp(-E/RT) \quad (8)$$

where k_0 ($\text{mmol}^{1-n} \text{cm}^{-3n+2} \text{s}^{-1}$) 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 vs $1/T$. However, the activation energy and k_0 were calculated by eq. (8). Figure 4 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 than that of Z2T. Based on eq. 8, an activation energy of 24.0 kcal mol⁻¹ and k_0 of $27.5 \text{ mmol}^{0.49} \text{ cm}^{-0.47} \text{ s}^{-1}$ were obtained for reduction in 10 mol% H₂-90 mol% N₂. This activation energy was close to the values (27-28 kcal mol⁻¹) reported by others for temperatures up to 700°C for ZnO powders (Hegedus and Kiss, 1966; Grunze and Hirschwald, 1974, 1975). For Z2T, the activation energy was 37.3 kcal mol⁻¹ and k_0 was $6.3 \times 10^4 \text{ cm s}^{-1}$.

Figure 5 shows that the initial reduction rates of various Zn-Ti-O materials with $(\text{Zn}/\text{Ti})_{\text{atomic}} \leq 3$ are similar to that of the sorbent Z2T. The solid Z9T, on the other hand, behaves like ZnO. Figure 6 shows the Arrhenius-type plots of the initial reduction rates of ZnO and Z9T. The activation energy for Z9T was 24.7 kcal mol⁻¹, similar to the value obtained for ZnO. This indicated that the same reaction mechanism was involved in the reduction of ZnO and Z9T,

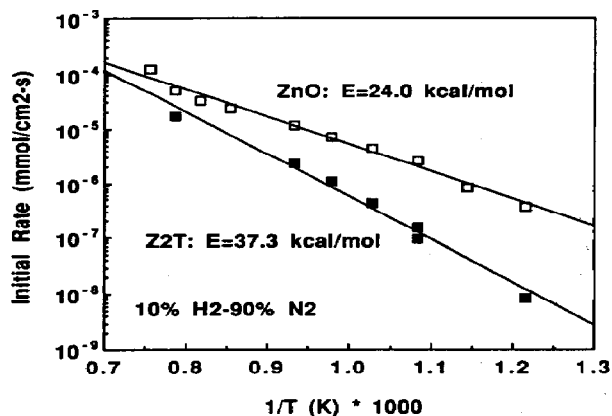


Fig. 4. Arrhenius-type plots of the initial reduction rates of ZnO and Z2T. Activation energies were calculated by eq. (8).

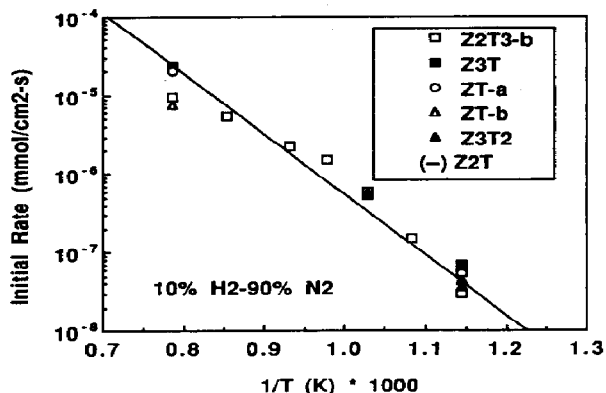


Fig. 5. Arrhenius-type plots of the initial reduction rates of various Zn-Ti-O solids.

which is not surprising considering that Z9T is comprised of 70 wt% ZnO and 30 wt% Zn₂TiO₄ as identified by XRD (Table 1). The major difference between ZnO and Z9T was the constant k_0 . For ZnO, k_0 was $27.5 \text{ mmol}^{0.49} \text{ cm}^{-0.47} \text{ s}^{-1}$, while for Z9T it was $17.4 \text{ mmol}^{0.49} \text{ cm}^{-0.47} \text{ s}^{-1}$.

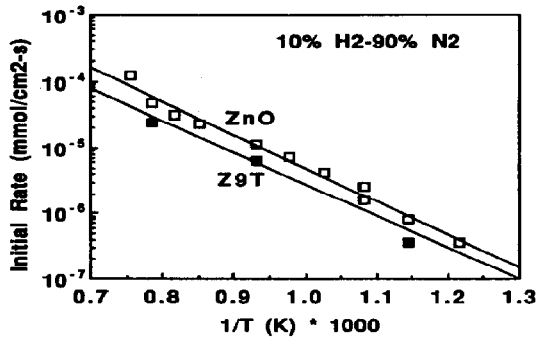


Fig. 6. Arrhenius-type plots of the initial reduction rates of ZnO and Z9T.

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 identify potential inhibitory effects on the reduction rate. For ZnO, a dramatic effect of H₂O on the reduction rate was observed with a concomitant change in the reaction order. Figure 7 shows the Arrhenius plots of ZnO reduction in the presence of various amounts of water vapor. The inclusion of 1 mol% H₂O 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. Figure 8 shows the effect of H₂ 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 one from its value of 0.51 in the absence of H₂O. In contrast, the reaction rate of Z2T remained first order. The activation energy was significantly higher in the presence of water vapor. With a gas containing 10 mol% H₂-3 mol% H₂O-87 mol% N₂, the activation energy was 43.9 kcal mol⁻¹ and k_0 was 9.27×10^5 cm s⁻¹. In contrast, the activation energy was only 24.0 kcal mol⁻¹ for the dry reduction.

Water also had an inhibitory effect on the reduction of Zn-Ti-O solids. Figure 9 shows the Arrhenius plots of Z2T reduction in the presence of 0, 3 and 8 mol% H₂O. However, the 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⁻¹ and k_0 changed to 3.36×10^5 cm s⁻¹. The new activation energy was approximately the same as the value obtained for ZnO reduction (43.9 kcal mol⁻¹) 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.

Similar inhibitory effects on ZnO reduction by water vapor have been observed by others (Hegedus and Kiss, 1966; Flytzani-Stephanopoulos *et al.*, 1987). From thermogravimetric studies, Hegedus and Kiss (1966) observed that as the water vapor content in a

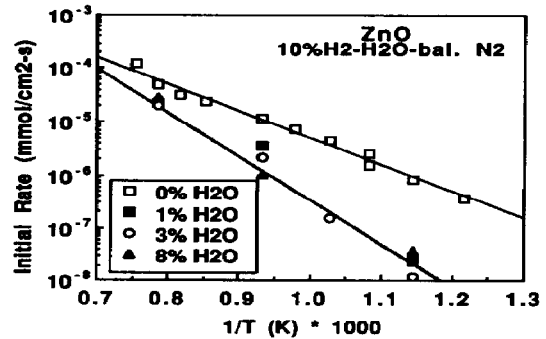


Fig. 7. Arrhenius-type plots of the initial reduction rates of ZnO in the presence of various amounts of H₂O.

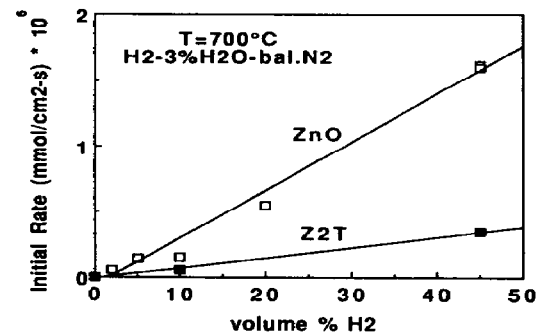


Fig. 8. Effect of hydrogen concentration on the initial reduction rate of ZnO and Z2T in the presence of 3% H₂O at 700°C.

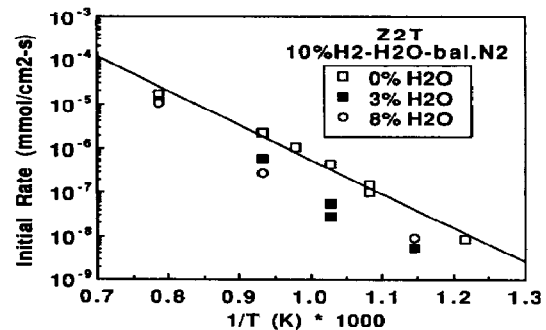


Fig. 9. Arrhenius-type plots of the initial reduction rates of Z2T in the presence of various amounts of H₂O.

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 ZnO reduction increased from 27.4 to 52 kcal mol⁻¹. 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 observed lower reduction rates for zinc oxide as well as zinc titanates in the presence of H₂O vapor.

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 Fig. 10. The reduction rates of Zn–Ti–O solids were lower than for bulk ZnO. The reduction rate steadily decreased as the relative amount of TiO₂ in the solid was increased. Unlike the dry reduction results (Fig. 2), no plateau is shown in Fig. 10 for solids with (Zn/Ti)_{atomic} ≤ 3. Comparative Arrhenius plots of ZnO, Z2T and Z2T3-b in the presence of H₂O are shown in Fig. 11. The activation energies of all solids were approximately the same (~44 kcal mol⁻¹). The difference in reactivity lies in the pre-exponential constant, *k*₀, as listed in Table 2. 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 m² g⁻¹) was reported to occur at rates lower (by tenfold) than that in this work. The self-inhibitory effect produced by the larger product H₂O 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 H₂O was varied from 7.0 × 10⁻³ to 5.9 × 10⁻²%. In our previous work, the product H₂O mole fraction was 6.5 × 10⁻³% based on the rate of H₂O production and the gas flow rate, while, in the present paper, the conditions of Fig. 2 correspond to H₂O 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 H₂–N₂ performed in this laboratory with ZnO single crystals characterized by low surface area (8.2 × 10⁻⁴ m² g⁻¹) and zero porosity yielded similar initial reduction rate to the low surface area (0.68 m² g⁻¹) bulk ZnO solid reported here (Lew, 1990).

Initial reduction rate of Zn–Ti–O solids: effect of partial sulfidation

ZnO and Z2T were 10–15% sulfided between 600 and 700°C in H₂–H₂S–N₂ gas mixtures. Subsequent reduction of the partially sulfided solids in 10 mol% H₂–90 mol% N₂ showed a lower initial reduction rate

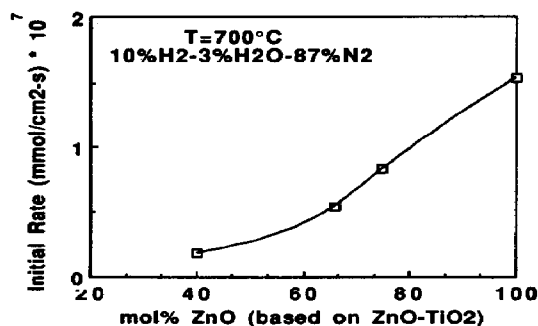


Fig. 10. A comparative plot of the initial reduction rates of various Zn–Ti–O materials reacted at 700°C in 10% H₂–3% H₂O–87% N₂.

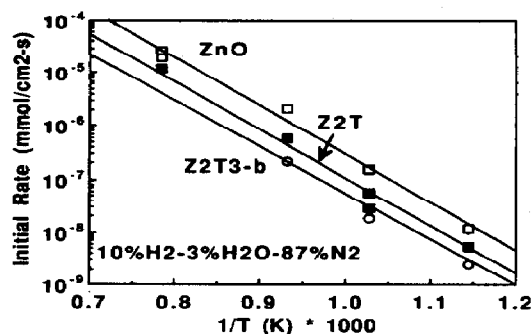


Fig. 11. Arrhenius-type plots of the initial reduction rates of ZnO, Z2T and Z2T3 in 10% H₂–3% H₂O–87% N₂.

Table 2. Values of *k*₀ for solid reduction in the presence of H₂O[†]

Solid	<i>k</i> ₀ (cm s ⁻¹)
ZnO	9.27 × 10 ⁵
Z2T	3.36 × 10 ⁵
Z2T3-b	1.31 × 10 ⁵

[†]Arrhenius plots shown in Fig. 11.

than reduction of the unsulfided solids. In these experiments, only the oxides were reduced. No reduction of ZnS was observed as measured by the weight change. As shown in Fig. 12, there appeared to be an inhibitory effect on reduction by H₂S similar to that found with water vapor. Figure 12(b) shows the ZnO reduction profiles. A sigmoidal shape profile is found for ZnO which has been partially sulfided. Initially (< 10 min) the reduction profiles of partially sulfided ZnO and of ZnO reduced in the presence of 3% H₂O 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 Fig. 12(a) 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, the reduction mechanism and the role of water vapor will be discussed. Hydrogen sulfide appears to play a role similar to that of water vapor.

Reduction model

From the kinetic measurements described above, 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°C) (Kesavulu and

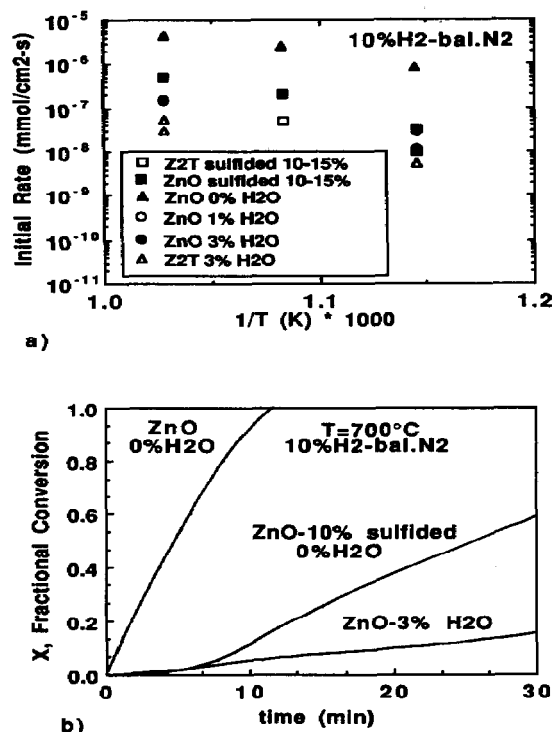


Fig. 12. Reduction of partially sulfided solids (a) comparison of the Arrhenius-type plots of the initial rate and (b) comparison of reduction profiles.

Taylor, 1960; Eischens *et al.*, 1962; Dent and Kokes, 1969; Boccuzzi *et al.*, 1978) has been reported in the literature. Since all the experiments performed in this study 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,

$$R_{0,A} = \frac{K_A C_{\text{H}_2}}{(1 + \sqrt{K_{\text{H}_2,A} C_{\text{H}_2}} + \sqrt{K_{\text{H}_2\text{O},A} C_{\text{H}_2\text{O}}})^2} \quad (9)$$

is obtained, where K_A is a constant related to the rate controlling step for the reaction, $K_{\text{H}_2,A}$ and $K_{\text{H}_2\text{O},A}$ 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 ($n \sim 0.51$ at 700°C), $(K_{\text{H}_2,A} C_{\text{H}_2})^{0.5}$ must be the same order of magnitude as one. In the presence of H_2O , sites A are poisoned. This is equivalent to $(K_{\text{H}_2\text{O},A} C_{\text{H}_2\text{O}})^{0.5} \gg 1$ or $(K_{\text{H}_2,A} C_{\text{H}_2})^{0.5}$. Thus, $R_{0,A}$ becomes small. For type B sites, a similar Langmuir-Hinshelwood equation is obtained:

$$R_{0,B} = \frac{K_B C_{\text{H}_2}}{(1 + \sqrt{K_{\text{H}_2,B} C_{\text{H}_2}} + \sqrt{K_{\text{H}_2\text{O},B} C_{\text{H}_2\text{O}}})^2} \quad (10)$$

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%, $(K_{\text{H}_2,B} C_{\text{H}_2})^{0.5}$ and $(K_{\text{H}_2\text{O},B} C_{\text{H}_2\text{O}})^{0.5} \ll 1$. Consequently, eq. (10) reduces to

$$R_{0,B} = K_B C_{\text{H}_2} \quad (11)$$

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

$$R_0 = R_{0,A} + R_{0,B} \quad (12)$$

In the absence of H_2O , reactions on type A sites is much faster than on type B sites. Thus, $R_0 \approx R_{0,A}$. At 700°C from the initial rates obtained at various hydrogen concentrations, the values of the constants are calculated and eq. (9) for $R_{0,A}$ becomes

$$R_{0,A} = \frac{[1.27 \times 10^{-2} (\text{cm s}^{-1})] C_{\text{H}_2}}{[1 + \sqrt{509.0 (\text{cm}^3 \text{mmol}^{-1}) C_{\text{H}_2}}]^2} \quad (13)$$

In the presence of H_2O , $R_{0,A} \approx 0$ and $R_0 \approx R_{0,B}$. For ZnO with the experimental results obtained with 10 mol% H_2 –3 mol% H_2O –87 mol% N_2 , eq. (11) becomes

$$R_{0,B} = 9.27 \times 10^5 (\text{cm s}^{-1}) e^{-43.9 (\text{kcal mol}^{-1})/RT} C_{\text{H}_2} \quad (14)$$

For Zn-Ti-O solids, the presence of titanium appears either to eliminate type A sites or modify their reactivity. The tenfold drop of the ZnO reduction rate in solids with $(\text{Zn}/\text{Ti})_{\text{atomic}} \leq 3$ 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 $(\text{Zn}/\text{Ti})_{\text{atomic}} \leq 3$, therefore, probably proceeds on another type of sites, labelled A', which are 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 (9) for type A' sites becomes

$$R_0 = 6.30 \times 10^4 \text{ (cm s}^{-1}\text{)} e^{-37.3 \text{ (kcal mol}^{-1}\text{)} / RT} C_{\text{H}_2} \quad (15)$$

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 Fig. 10, 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. (14) 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 (Fig. 2), 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 (Bocuzzi *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.

Reduction conversion profiles of bulk Zn–Ti–O solids

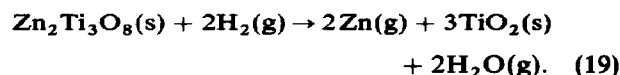
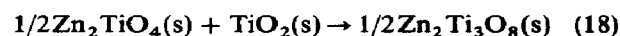
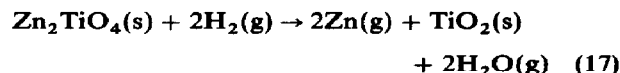
Typical experimental conversion–time profiles for ZnO and Z2T at 650°C are shown in Fig. 13. The following fractional conversion is defined as

$$X = (W_i - W) / (W_i - W_f^0) \quad (16)$$

where W is the weight, W_i is the initial weight, and W_f^0 is the final weight at complete conversion. For ZnO, W_f^0 is equal to zero. W_f^0 is the weight of the remaining TiO₂ for Zn–Ti–O solids. For both ZnO and Z2T,

the reaction rates remained relatively constant up to a high level of conversion. For Z2T reduction, a product layer of TiO₂ is formed. Since the ratio of the solid product (TiO₂) molar volume to the solid reactant (Zn₂TiO₄) molar volume is only 0.41, a porous product layer is formed. Based on 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. Sufficient quantities of materials for analyses were obtained by reacting 40–50 mg of solids in the TGA. Table 3 lists the results of the XRD analyses of various partially reduced solids. The reactions were performed at 650°C in 10 mol% H₂–90 mol% N₂. For the solid Z2T, the following reactions appeared to occur during reduction:



No corresponding change in the reaction rate accompanied the phase change from Zn₂TiO₄ to Zn₂Ti₃O₈. At conversion higher than 66%, the only reactive phase present was Zn₂Ti₃O₈. As shown in Fig. 13, no noticeable change in the reduction rate was observed. For the solid Z2T3-b, consisting of ZnTiO₃ and TiO₂ (Table 1), ZnTiO₃ reacted directly

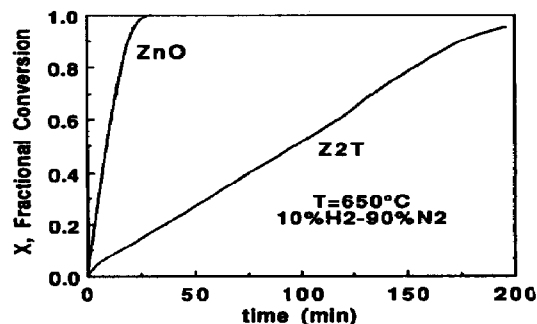


Fig. 13. Comparison of the experimental reduction profiles of ZnO and Z2T at 650°C in 10% H₂–90% N₂.

Table 3. XRD analyses of reduced Zn–Ti–O solids[†].

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

[†] Reduced in the TGA at 650°C in 10 mol% H₂–90 mol% N₂.

with H_2 to form $Zn(g)$ and $TiO_2(s)$. No intermediate chemical phases were detected. Although these XRD analyses revealed that the crystalline phase transformations of Zn_2TiO_4 and $ZnTiO_3$ were different, these differences did not affect the initial reduction rate as discussed previously.

After partial reduction of Zn-Ti-O solids, changes in the color of the solids were observed. ZnO which was initially white, 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 14 shows the SEM micrographs of Z9T unreacted and

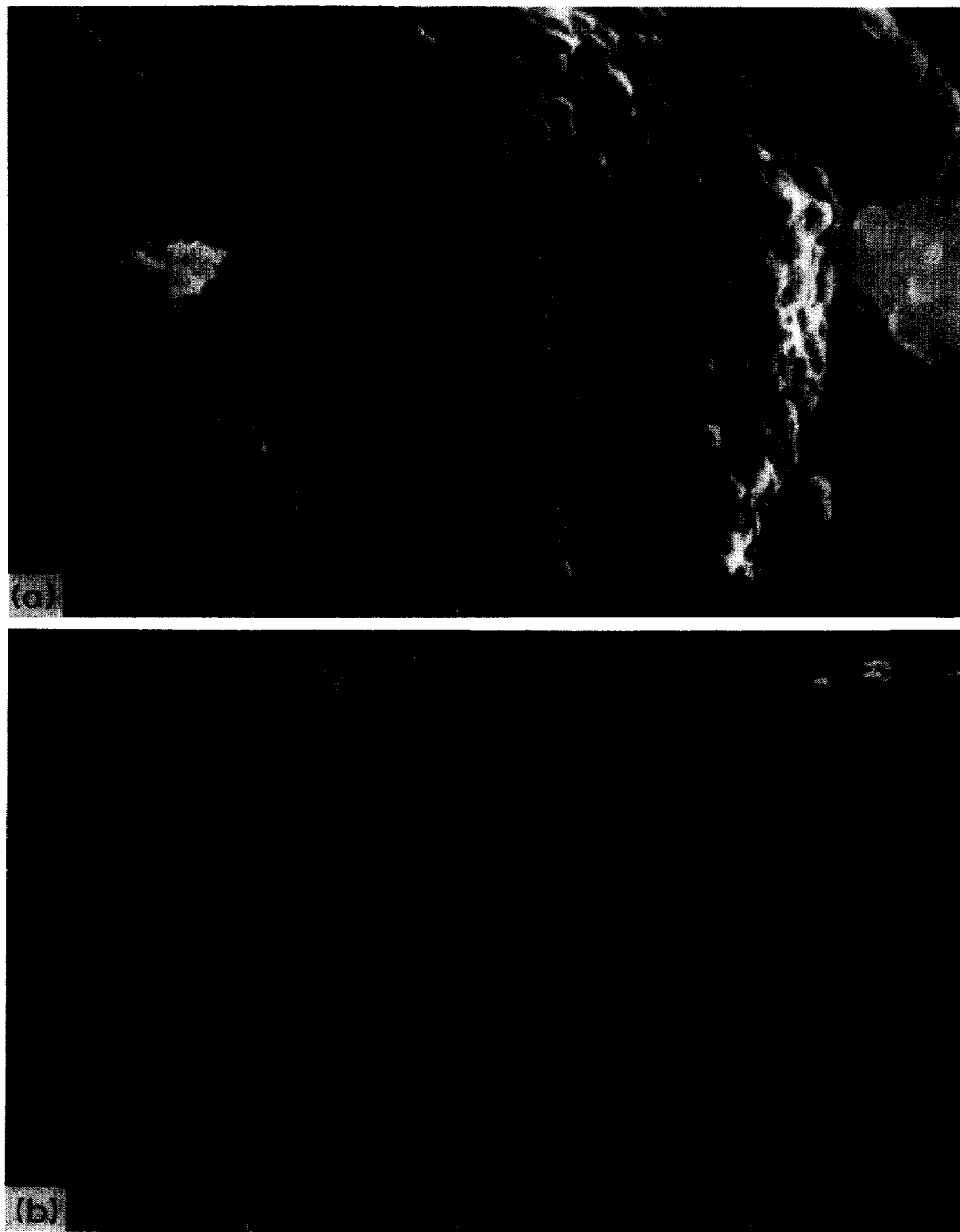


Fig. 14. SEM micrographs of Z9T calcined at $1000^{\circ}C$: (a) unreacted and (b) 45% reduced at $650^{\circ}C$ in 10% H_2 -90% N_2 .

partially reduced (45%) at 650°C in 10 mol% H₂-90 mol% N₂. Z9T is composed of a mixture of ZnO and Zn₂TiO₄. The unreacted solid [Fig. 14(a)] is composed of closely packed crystals (0.1-0.2 μm radius). After partial reduction [Fig. 14(b)], 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 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. As can be seen in Fig. 14(b), the sizes of the remaining crystals were relatively unchanged after 45% conversion.

SUMMARY AND CONCLUSIONS

A detailed study of hydrogen reduction of bulk Zn-Ti-O materials has been presented in this paper, 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 (zero % 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⁻¹, 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⁻¹ for both ZnO and Zn-Ti-O solids. Increasing the relative amount of TiO₂ from zero 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 (Zn/Ti)_{atomic} ≤ 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 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. Work along these lines is presently in progress.

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