

HOT GAS DESULFURIZATION BY ZINC OXIDE-TITANIUM DIOXIDE REGENERABLE SORBENTS

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ABSTRACT

Comparative kinetic of reduction and sulfidation of zinc oxide and zinc titanate materials were carried out in a thermogravimetric apparatus over the temperature range of 600-1000°C (reduction) and 500-700°C (sulfidation). Both dry as well as wet (H₂O) reactant gas mixtures of H₂-N₂ were used in reduction. For sulfidation, gas mixtures of H₂-H₂S-N₂ were tested. Sulfidation reactivity and reduction stability were correlated with active sorbent crystal phase, e.g. ZnO, Zn₂TiO₄, ZnTiO₃, and Zn₂Ti₃O₈. TiO₂ addition into ZnO retarded reduction rate.

INTRODUCTION

The removal of H₂S to sufficiently low levels from coal-derived gas streams at elevated temperatures is crucial for the 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. Previous studies (1,2) have investigated zinc oxide (ZnO) as a regenerable sorbent. The thermodynamic equilibrium for sulfidation of ZnO is quite favorable, yielding desulfurization down to a few ppm H₂S. However, a difficulty with all sorbents containing zinc oxide is some reduction to volatile elemental zinc at temperatures above 600°C. The instability of zinc oxide in a reducing atmosphere limits its operating temperature to approximately 600°C.

Recent sorbent developmental work has shown that mixtures of ZnO with TiO₂ in the form of compounds such as Zn₂TiO₄ or ZnTiO₃ can be used at higher desulfurization temperatures than pure ZnO without appreciable zinc loss by reduction and vaporization of zinc metal (3-5). The decrease in reduction was attributed to the formation of the mixed ZnO compounds.

In this study, the behavior of pure ZnO and several ZnO-TiO₂ sorbents with a molar ratio of ZnO to TiO₂ ranging from 2:3 to 9:1 was examined in both reduction with H₂-N₂ at 600-1000°C and sulfidation with H₂S-H₂-N₂ at 500-700°C. Detailed kinetic studies of a sorbent containing 2 ZnO:1 TiO₂ and of pure ZnO were conducted in reduction and sulfidation experiments. In addition, the effect of H₂O on the reduction behavior was studied. H₂O is usually a significant component of coal-derived gases. H₂O content varying from 50 vol% in a fixed bed Lurgi gasifier to 10 vol% in a fluidized bed KRW gasifier is typical (6).

EXPERIMENTAL

Model sorbent materials were prepared by the amorphous citrate technique (7) which involves the complexation of aqueous solutions of the metal salts in desired proportions with citric acid followed by rapid dehydration, pyrolysis and air calcination at various temperatures. The major advantage of this preparation technique is the production of bulk mixed oxides with good interdispersion and homogeneity. Additionally, mixed oxide particles produced by this technique are highly macroporous, and, thus, amenable to independent measurements of chemical kinetic rates and product layer diffusion (in the absence of pore diffusion). A typical material produced by this method is shown in Figure 1.

The sorbents were characterized by several bulk and surface analysis techniques. X-ray diffraction (XRD) identification of crystalline phases present in the mixed oxide sorbents was performed using a

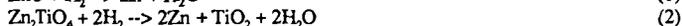
CuK α source by a Rigaku RU300 instrument. Specific surface area was measured with a Micromeritics Flow Sorb II 2300 BET apparatus. The pore volume and pore size distribution were determined by a Micromeritics Autopore 9200.

Reactions were performed in a Cahn 113-X thermogravimetric apparatus (TGA) equipped with a Cahn 2000 electrobalance, an electric furnace, a Micricon temperature controller, and a Bascom Turner data acquisition system. The balance section of the TGA is constantly purged with nitrogen gas flowing at a known flow rate. The reactant gas is introduced into the apparatus through a side-stream. A thin layer of sample (typically 2-4 mg and -115/+170 mesh size) was placed on a quartz pan suspended by a quartz hangdown wire.

RESULTS AND DISCUSSION

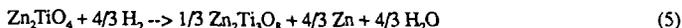
Sorbent Reduction

Reduction studies of ZnO neat and several ZnO-TiO₂ materials with various zinc to titanium ratios were carried out in the TGA. A few of the solids studied are listed in Table 1. Several different crystalline phases were identified in the mixed oxide sorbents, namely, ZnO, Zn₂TiO₄, Zn₂Ti₃O₈, and ZnTiO₃. The overall reduction reactions that can take place are:



The initial rate of reduction for samples with different composition of ZnO-TiO₂ is shown in Figure 2. The rates for two temperatures, 600°C and 700°C, in 10% H₂-90% N₂ are depicted. The initial rate is defined as the rate of Zn loss (mmol/s) normalized with the total surface area of the sample (cm²). Z2T (Table 1) which is composed of Zn₂TiO₄ corresponds to 66.7% ZnO in Figure 2. 0% ZnO is equivalent to 100% TiO₂. In agreement with previous studies (3-5), lower reduction rates are observed with zinc titanates. With as little as 10% TiO₂ (Z9T in Table 1), a noticeable decrease in the rate is observed. As shown in Figure 2, the reduction rate for the sample with 10% TiO₂ is approximately twice as slow as ZnO neat. For a sample with 25% TiO₂ (Z3T), the reduction rate is approximately 10 times slower than ZnO neat. This is true even though 33% of the zinc in Z3T is present as ZnO. The striking observation is that as the amount of TiO₂ increases above 25%, the reduction rate remains relatively unchanged. This is true regardless of the fact that the crystalline phases present vary with sorbent composition.

From XRD analyses of partially reduced Z2T3, only the phases of ZnTiO₃ and TiO₂ were found. Thus, reduction of ZnTiO₃ proceeds directly by reaction (4). The partially reduced sorbent Z2T is composed of a mixture of Zn₂TiO₄ and Zn₂Ti₃O₈. Thus, reduction of Zn₂TiO₄ proceeds by:



The Zn₂Ti₃O₈ formed is then reduced according to reaction (3). Zn₂Ti₃O₈ has a defect spinel structure. It is, thus, not surprising that abstraction of Zn atoms from Zn₂TiO₄, which is also a spinel, produces Zn₂Ti₃O₈. In both Z2T and Z2T3, reactions occur by the reduction of different initial crystalline phases and intermediates. The fact that the initial reduction rate is the same for both sorbents implies that the reduction kinetics are independent of the type of zinc titanate compound present.

Z2T was chosen for further studies of the reduction kinetics. Comparisons were made with ZnO. The reaction order with respect to H₂ concentration was determined at 700°C in a mixture of H₂ and N₂ gases. For Z2T, the reaction order is unity. However, for ZnO, it is 0.5. In Figure 3, an Arrhenius plot is shown using 10% H₂ and 90% N₂. In the temperature range of study (600-1000°C), the reduction rate of

ZnO is greater than Z2T. The apparent activation energy for Z2T reduction is 37 kcal/mol, while for ZnO, it is 24 kcal/mol. The activation energy (E) was determined by the rate equation:

$$r = k_0 e^{-E/RT} (C_{H_2})^n \quad (6)$$

The presence of H₂O drastically changed the reduction kinetics of ZnO. The reaction order for ZnO changed from 0.5 with 0% H₂O-H₂-N₂ to 1.0 in the presence of 3% H₂O-H₂-N₂. But, for Z2T, the reaction order was unaffected by the presence of H₂O. The reduction rate of ZnO decreased significantly when H₂O was present in the reactant stream. Figure 4 shows an Arrhenius plot for ZnO reduction in the presence of various amounts of H₂O. A large change in reduction rate was observed when the amount of H₂O was changed from 0% to 1%. With 3% H₂O, a much smaller drop in reduction rate took place compared to the change observed when the H₂O content was increased from 0% to 1%. At 8% H₂O, again only small changes in the reduction rate were observed.

In contrast to the effect of H₂O on ZnO reduction, a smaller decrease in reduction rate was observed for Z2T. In Figure 5, the Arrhenius plot for Z2T reduction in the presence of various amounts of water vapor is presented. The activation energy changed from 37 kcal/mol in the absence of H₂O to 44 kcal/mol in the presence of 3% H₂O. In the presence of 8% H₂O, as in the case of ZnO, only small additional changes in the reduction rate were observed. Figure 6 shows a comparison of the Arrhenius curves for ZnO and Z2T reduction in the presence of 3% water vapor. The activation energies (44 kcal/mol) for both sorbents were the same. ZnO reduction rate was 2-3 times faster than Z2T. Also, the reaction orders of ZnO and Z2T were both unity.

To explain the experimental data for both ZnO and Z2T reduction a kinetic model was developed. The inhibition of reduction by water vapor is presumably a result of competition by hydrogen and water vapor for active sites on the samples. This is in good agreement with an earlier study (8) carried out by Dent and Kokes who observed lower hydrogen adsorption on zinc oxide pre-adsorbed with H₂O. To explain the inhibition pattern observed in the present study, a two-site model similar to one found in the literature (9) is postulated. Two types of sites (Type A and Type B) on ZnO are involved in hydrogen adsorption. Other researchers (e.g. 8, 10-13) have also observed the presence of two hydrogen adsorption sites on zinc oxide at low temperatures (25-200°C). One is known to adsorb hydrogen very rapidly but is also poisoned by H₂O. The other site involves initially fast hydrogen adsorption followed by much slower absorption and is apparently not affected by H₂O. For this study, Type A sites are postulated to be very reactive and responsible for most of the reduction on ZnO. However, Type A sites also appear to be easily poisoned by H₂O. In the presence of H₂O, these sites are blocked and will not play a role in reduction. Type B sites are less reactive than Type A sites but are not as easily poisoned.

With a Langmuir-Hinshelwood model, the rate expressions for reduction are written as:

$$r_A = k_A C_{H_2} / (1 + K_{A,H_2}^{1/2} C_{H_2}^{1/2} + K_{A,H_2O}^{1/2} C_{H_2O}^{1/2})^2 \quad (7)$$

$$r_B = k_B C_{H_2} / (1 + K_{B,H_2}^{1/2} C_{H_2}^{1/2} + K_{B,H_2O}^{1/2} C_{H_2O}^{1/2})^2 \quad (8)$$

where $K_{A,H_2O} \gg K_{A,H_2}$, $K_{B,H_2}^{1/2} C_{H_2}^{1/2} \ll 1$, and $K_{B,H_2O} \ll K_{A,H_2O}$. The overall reaction rate is

$$r = r_A + r_B \quad (9)$$

In the absence of H₂O, the reduction rate for ZnO is:

$$r = r_A = k_A C_{H_2} / (1 + K_{A,H_2}^{1/2} C_{H_2}^{1/2})^2 \quad (10)$$

In the presence of H₂O, it becomes:

$$r = r_B = k_B C_{H_2} / (K_{B,H_2O}^{1/2} C_{H_2O}^{1/2})^2 \quad (11)$$

With Z2T, it is postulated that there are very few Type A sites. The reaction rate is due mainly to Type B sites. This is possible if similarities to the previous hydrogen adsorption studies (8,10-13) at low temperatures are drawn. The sites with rapid hydrogen adsorption are believed (10-11) to consist of clusters of adjacent Zn cations and at least one reactive O anion on a reconstructed polar face. If Ti cations are present in these sites, they may disrupt the interaction between ions necessary for active sites. It is not certain that similarities can be drawn to the previous studies since hydrogen adsorption on zinc oxide was conducted at considerably lower temperatures (25-200°C) than the temperatures (600-1000°C) in this present work. However, several similar characteristics are present, such as high reactivity and poisoning by H₂O.

Sorbent Sulfidation

Figure 7 presents the results of sulfidation experiments with different compositions of ZnO-TiO₂. The experiments were conducted with 2% H₂S-1% H₂-97% N₂ at 700°C. Comparative reduction experiments are also depicted in Figure 7. Similar to the results observed for reduction, the initial rate of sulfidation does not appear to be affected by the type of zinc titanate compounds (Zn₂TiO₄ and ZnTiO₃) or amount of TiO₂ (33-73%) present. The initial rate of sulfidation of ZnO is only about 1.5 times higher than zinc titanates. In contrast, the initial reduction rate of ZnO is about 10 times greater than that of zinc titanates.

More detailed sulfidation studies were conducted with Z2T and ZnO to determine kinetic parameters. The overall reactions considered are:



The reaction order with respect to hydrogen sulfide was unity for both ZnO and Z2T at 700°C. An Arrhenius plot for both sorbents is drawn in Figure 8. The activation energies for both sorbents are approximately the same (8-9 kcal/mol). Because of the similarity in reaction order and activation energy for ZnO and Z2T, the conclusion is made that sulfidation of Z2T (Zn₂TiO₄) proceeds by the same rate-controlling mechanism as ZnO. XRD analyses of partially sulfided (48 mole % converted) Z2T have identified a mixture of Zn₂TiO₄, Zn₂Ti₃O₇, α-ZnS, and β-ZnS. Thus, the similarity in kinetic parameters is not due to decomposition of Zn₂TiO₄ to ZnO and TiO₂. The low activation energy is suggestive of chemisorption of H₂S being the rate-controlling mechanism.

In Figure 8, the effect of various amounts of H₂ in the reactant gases is also shown. Hydrogen is added to the reactant gases because it is a major component of coal derived-gases and also because it can inhibit the decomposition of H₂S at these temperatures (500-700°C). The amount of hydrogen was varied from 0% to 10% H₂S. No significant change in the initial rate was observed for both ZnO and Z2T. This indicates that Type A hydrogen adsorption sites are different from hydrogen sulfide adsorption sites on ZnO. If the two types of sites were the same, the Langmuir-Hinshelwood expression for sulfidation would be:

$$r = k_{A,H_2S} C_{H_2S} / (1 + K_{A,H_2S} C_{H_2S} + K_{A,H_2}^{1/2} C_{H_2}^{1/2}) \quad (14)$$

Since the reaction order with respect to H₂S is unity, K_{A,H₂S} C_{H₂S} << 1, while K_{A,H₂}^{1/2} C_{H₂}^{1/2} is of order unity. Thus, increasing hydrogen concentration would decrease the sulfidation rate due to competitive adsorption of hydrogen. Since no change in rate was observed for ZnO sulfidation, it may be concluded that hydrogen sulfide adsorption sites are not the same as hydrogen adsorption sites. This can also explain why zinc titanate materials have such low reduction rates, without a similar decrease in sulfidation rates. Zinc titanate materials lack the highly reactive sites (Type A sites), which are crucial for reduction but not for sulfidation.

CONCLUSIONS

This study has demonstrated the advantages of ZnO-TiO₂ sorbents. As little as 25 wt % of TiO₂ (present as a zinc titanate compound) will give the same decrease in reduction rate as significantly more TiO₂ (60 wt%). In contrast to ZnO neat, a significantly lower reduction rate (approximately 10 times lower at 700°C) was observed in ZnO-TiO₂ materials in a H₂-N₂ reaction gas mixture. The presence of different zinc titanate compounds (i.e. Zn₂TiO₄, ZnTiO₃, or Zn₂Ti₃O₈) does not noticeably change the reduction rate. The presence of water vapor in the reactant gas will strongly inhibit ZnO reduction but will not have the same effect on ZnO-TiO₂ materials. ZnO reduction is only about 2-3 times faster than ZnO-TiO₂ in the presence of H₂O. It is postulated that the difference in reduction rate is due to the existence of highly reactive sites on ZnO which are poisoned by H₂O.

There is not a large difference in the initial rate of ZnO-TiO₂ sulfidation compared with ZnO sulfidation under identical reaction conditions. The initial sulfidation rate of ZnO is only about 1.5 times faster than for ZnO-TiO₂ sorbents. Because of similar kinetic parameters (i.e. activation energy and reaction order), similar sulfidation mechanisms are believed to be involved for both ZnO and ZnO-TiO₂. Again, no significant difference in sulfidation rate is observed with different zinc titanate compounds (i.e. Zn₂TiO₄ or ZnTiO₃).

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Table 1. Physical and Chemical Properties of Sorbents^a

Sorbent Designation	Zn/Ti (atomic ratio)	surface area (m ² /g)	pore volume (cm ³ /g)	Crystalline Phases (wt %)				
				ZnO	Zn ₂ TiO ₄	ZnTiO ₃	Zn ₂ Ti ₃ O ₈	TiO ₂
ZnO	---	2.4	1.2	100	0	0	0	0
Z9T ^b	9/1	1.0	NA	72	28	0	0	0
Z3T	3/1	7.5	0.9	28	72	0	0	0
Z2T	2/1	4.1	0.7	0	100	0	0	0
Z3T2	3/2	2.2	0.7	0	82	18	0	0
ZT	1/1	1.6	0.6	0	0	45	55	0
Z2T3	2/3	1.3	0.3	0	0	83	0	17

^a calcined at 720°C; ^b calcined at 1000°C

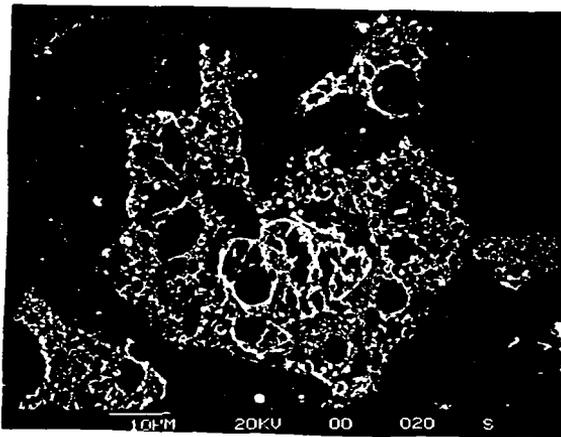


Figure 1. SEM micrograph showing the macroporous structure of a ZnO sorbent prepared by the amorphous citrate technique with pore volume=1.2 cm³/g and surface area=2.4 m²/g; sorbent cross-section shown.

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				ZnO	Zn ₂ TiO ₄	ZnTiO ₃	Zn ₂ Ti ₃ O ₈	TiO ₂
ZnO	---	2.4	1.2	100	0	0	0	0
Z9T ^b	9/1	1.0	NA	72	28	0	0	0
Z3T	3/1	7.5	0.9	28	72	0	0	0
Z2T	2/1	4.1	0.7	0	100	0	0	0
Z3T2	3/2	2.2	0.7	0	82	18	0	0
ZT	1/1	1.6	0.6	0	0	45	55	0
Z2T3	2/3	1.3	0.3	0	0	83	0	17

^a calcined at 720°C; ^b calcined at 1000°C

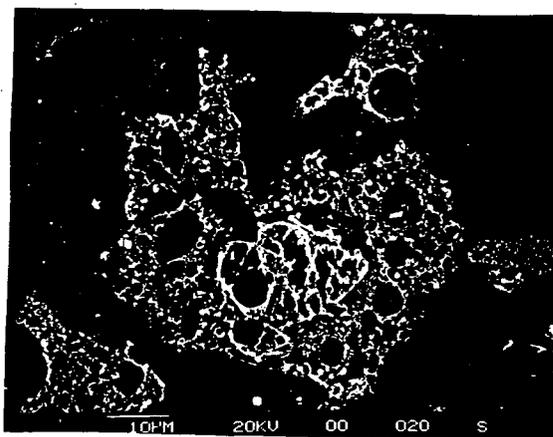


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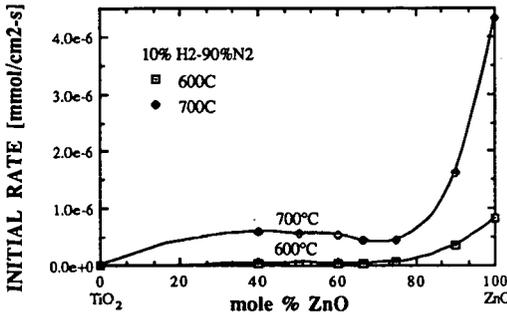


Figure 2. Comparison of initial rate of reduction of samples containing different amounts of ZnO and TiO₂.

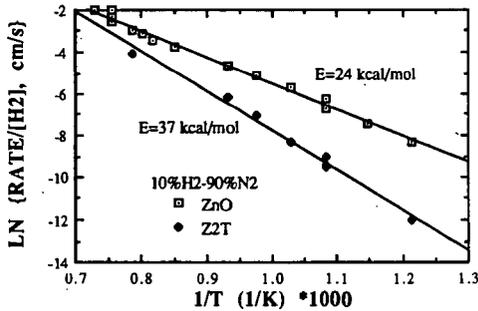


Figure 3. Arrhenius plot comparing reduction of ZnO with that of Z2T in 10%H₂-90%N₂ between 600-1000°C.

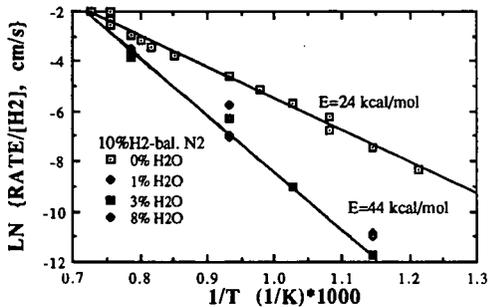


Figure 4. Arrhenius plot of ZnO reduction with various amounts of H₂O.

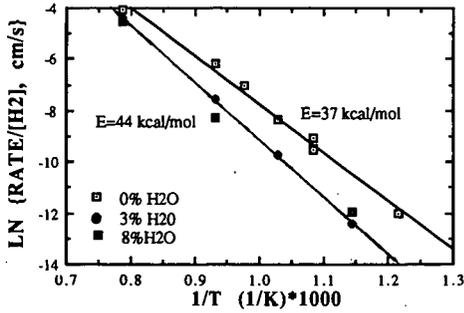


Figure 5. Arrhenius plot of Z2T reduction with various amounts of H₂O.

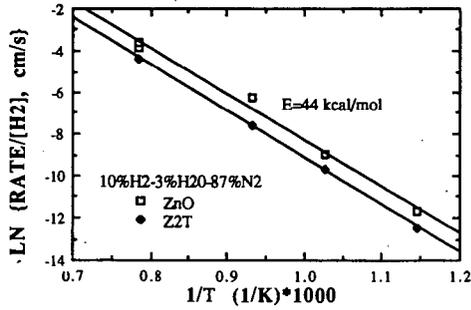


Figure 6. Comparison of ZnO and Z2T reduction in 10%H₂-3%H₂O-87%N₂.

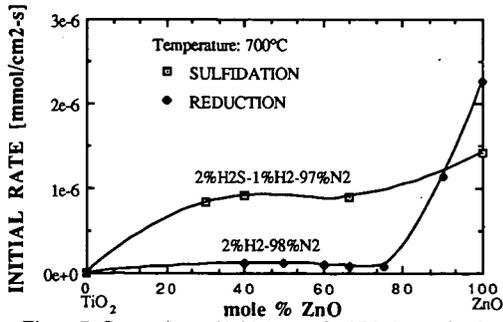


Figure 7. Comparison of initial rate of sulfidation and reduction of samples containing different amounts of ZnO and TiO₂.

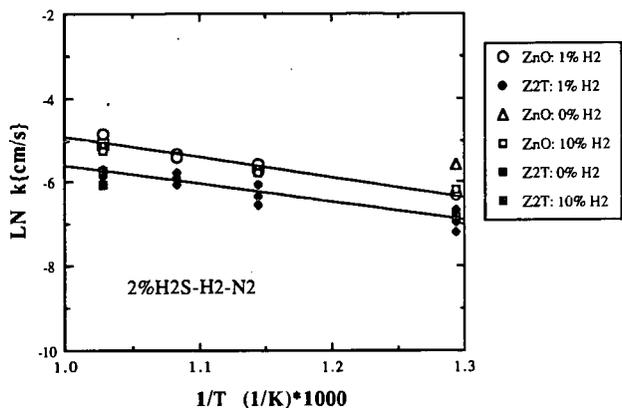


Figure 8. Arrhenius plot of ZnO and Z₂T sulfidation for various hydrogen concentrations . Rate= kC_{H_2S}