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SULFIDATION AND REDUCTION OF ZINC TITANATE AND ZINC OXIDE SORBENTS FOR INJECTION IN GASIFIER EXIT DUCTS

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ABSTRACT

The sulfidation reaction kinetics of fine particles of zinc titanate and zinc oxide with H_2S were studied in order to test the potential of the sorbent injection hot-gas desulfurization process. Fine sorbent particles with diameter between 0.3 and 60 μm were sulfided with H_2S and/or reduced with H_2 in a laminar flow reactor over the temperature range of 500-900 °C. Sulfidation/reduction conversion was compared for different particle sizes and sorbents with various porosities and atomic ratios of Zn and Ti. In reduction of ZnO with H_2 and without H_2S, significant amount of Zn was formed and vaporized, while the presence of H_2S suppressed elemental Zn formation. This suggests that H_2S may suppress the surface reduction of ZnO and/or gaseous Zn may react with H_2S homogeneously and form fine particles of ZnS. Formation and vaporization of elemental Zn from zinc titanate sorbents was slower than from zinc oxide with and without H_2S.

MASTER

INTRODUCTION

An advanced gas cleanup process, i.e. hot gas desulfurization and dust removal, is required for the high efficiency and low emission levels of the integrated coal gasification combined-cycle power generation (IGCC) and the gasification-molten carbonate fuel cell (MCFC) system. Among several metal oxides which react with H_2S to form solid metal sulfides, ZnO has been studied extensively as a desulfurization sorbent of H_2S. Though ZnO is a potential candidate as a sorbent material with quite favorable thermodynamic equilibrium of sulfidation with H_2S, it has a major problem, namely, formation and vaporization of elemental Zn by reduction reaction with H_2 and CO in the coal derived gas. More recently, mixed oxide sorbents, particularly Zn-Ti-O, have been considered as more promising sorbents combining high desulfurization performance, easiness of regeneration, and high stability.

The reaction schemes with ZnO and Zn-Ti-O sorbents are as follows;

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DISCLAIMER

$$\begin{array}{lll}
\text{H2S Uptake ;} & ZnO + H_2S \rightarrow ZnS + H_2O & (1) \\
 & Zn_xTi_yO_x + yO_2 + xH_2S \rightarrow xZnS + yTiO_2 + xH_2O & (2) \\
\text{Regeneration;} & 2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2 & (3) \\
 & xZnS + yTiO_2 + (3x/2)O_2 \rightarrow Zn_xTi_yO_x + yO_2 + xSO_2 & (4) \\
\text{Reduction ;} & ZnO + H_2 \text{ (or CO)} \rightarrow Zn + H_2O \text{ (or } CO_2\text{)} & (5) \\
 & Zn_xTi_yO_x + yO_2 + xH_2 \text{ (or xCO)} \rightarrow xZn + yTiO_2 + xH_2O \text{ (or } xCO_2\text{)} & (6)
\end{array}$$

However, loss of Zn by reduction, long-term stability, and mechanical durability of the material are still problems in any type of reactor, such as moving bed (granular sorbent), fluidized bed (powdered sorbent), and fixed bed (particle or monolith).

One possible way to avoid all the problems with H_2S sorbents mentioned above is the sorbent injection process. Fig. 1 shows the process schematic of the sorbent injection process. In this process, fine powder of the sorbent is injected into the reaction section, actually a gas pipe, and entrained with the coal derived gas. The sorbent is then captured by a porous ceramic micro filter, on which desulfurization reaction still takes place. The filter is backflushed intermittently, and the sorbent removed from the filter is entrained and regenerated by regeneration (oxidizing) gas and sent to a lock hopper prior to re-injection.

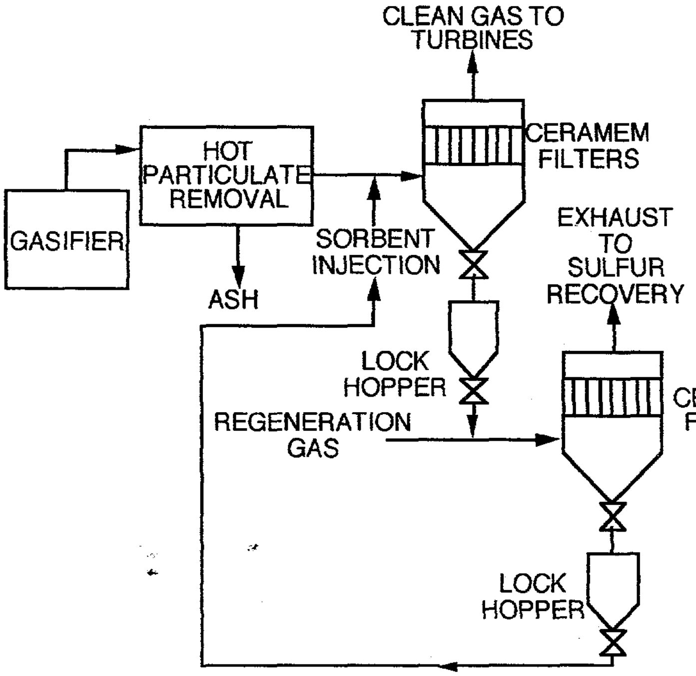


Fig. 1 A process schematic of the sorbent injection process (CeraMem Corporation)

Sorbent injection process in conjunction with a porous ceramic micro filter which can collect particles as small as less than 1 micron in diameter may be a solution to many of the problems with Zn-based sorbent because 1) the sorbent injection process can collect fine zinc sulfide formed with gaseous reaction of Zn vapor and H_2S, thus avoiding the loss of Zn; 2) fine powder encounters no attrition problem in duct; and 3) very fine particle size of the sorbent and the possible pathway of gaseous reaction between H_2S and Zn vapor may enhance the total desulfurization reactivity as suggested in a previous study [1]. Fig. 2 shows an anticipated reaction scheme which includes two reaction pathways, i.e. a solid-gas reaction between ZnO and H_2S, and a gas phase reaction between Zn vapor and H_2S.

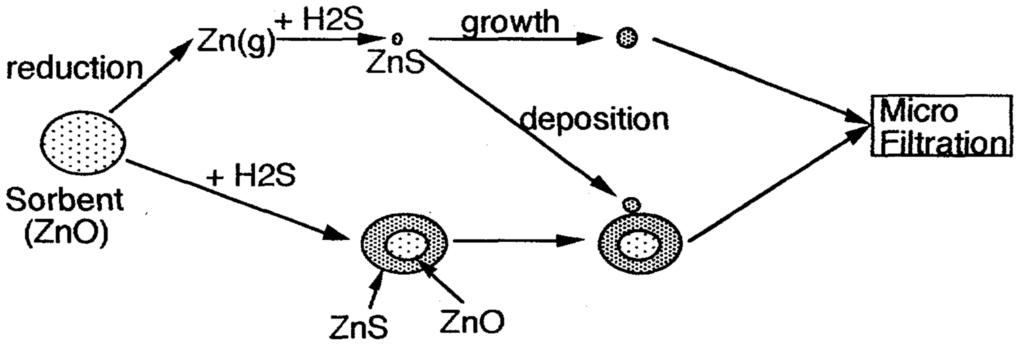


Fig. 2 An anticipated reaction scheme of a single sorbent particle

EXPERIMENTAL METHODS

Preparation of Sorbents

In the sorbent injection process, very fine powder of sorbent can be used and the micro structure of the sorbent material is expected not to affect much its reactivity. One of the objectives of this study is to compare several kinds of sorbents in terms of reactivity and to determine if low surface area material can be used. Therefore, in this study, a ZnO prepared at Massachusetts Institute of Technology by the complexation method[1] was used as the standard sorbent and compared with commercial materials, i.e. ZnO obtained from Johnson Matthey and $ZnTiO_3$ from Pfaltz and Bauer. As a Zn-Ti-O sorbent, and L-3140 sorbent of United Catalysts Inc.

Physical and Chemical Analysis of Sorbents

(i) Physical analysis. The pore size distributions and the surface areas of the sorbents were measured using a Micromeritics Autopore 9200 Mercury Porosimeter and a Micromeritics Flow Sorb 2300 BET apparatus, respectively.

(ii) Chemical analysis. Sulfidation conversion of the reacted ZnO and Zn-Ti-O sorbents in the drop-tube furnace assembly were measured using a Cahn System 113-X thermogravimetric analyzer (TGA). This analysis was based on the weight change of the sorbents upon regeneration reaction at 750°C in 6 vol% O_2 in N_2. The effect of elemental Zn formed by reduction with H_2 in the reactant gas and adsorbed materials such as H_2S or H_2O were subtracted by heating the sample to stable weight at 750°C in N_2 before introducing O_2.

Drop-Tube Furnace Experiments

Fig. 3 shows the flow schematic of the drop-tube test facility. The reactor is a 1.5 inch I.D. quartz tube and the feeder probe through which the sorbent is entrained by carrier gas is a 1/8 inch O.D. quartz tube. The collection probe is made of stainless steel and water-cooled. The collection probe has a porous inner wall through which N_2 gas was emitted into the reacted gas for quenching.

The reactant gas, a simulated coal gasifier-exit gas, comprises H_2S, H_2, CO_2, and N_2. Other components such as CO, H_2O, and trace of COS are omitted from the present experiments. Each gas component was fed from a gas cylinder and the flow rate was controlled by a mass flow controller. Sorbent particles were previously classified in a known size range and fed into a drop-tube down-flow reactor at a constant rate through a particle feeder. CO_2 or He was mainly used as the carrier

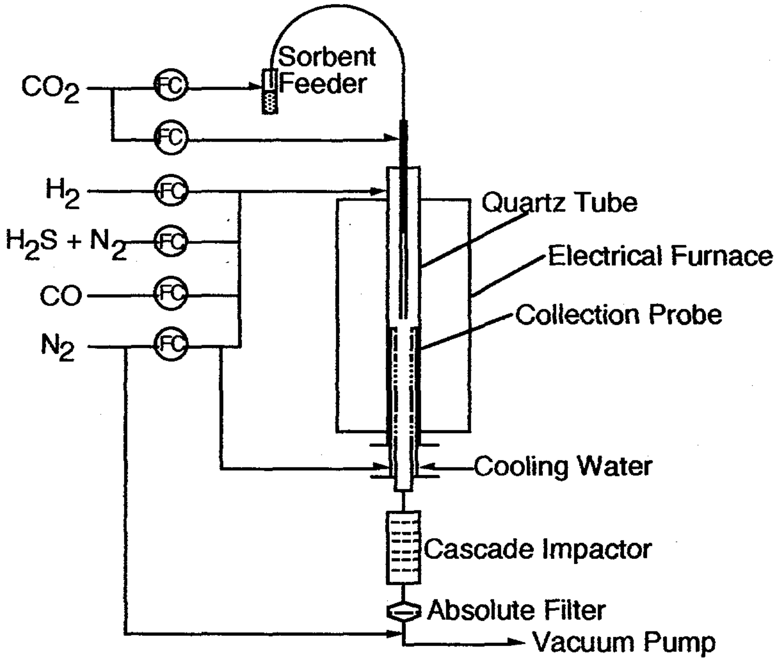


Fig. 3 The flow schematic of the drop-tube test facility

gas of the sorbent. The sorbent contacted the reactant gas for a certain distance, i.e. a certain contact time. In addition to the reactant gas, N_2 was fed to the collection probe for quenching the reacted gas. The reacted gas and N_2 from the collection probe were then led to a cascade impactor, University of Washington Mark 3 type, in which sorbent particles contained in the gas flow were classified according to the particle size into seven stages and a final paper filter.

By using a drop-tube reactor in conjunction with a cascade impactor, sulfidation conversion of different size sorbent particles can be measured separately because the cascade impactor size-classifies the particles in the reacted gas flow. Furthermore, the change of size distribution of the sorbent after the reaction could provide information on the reduction of ZnO and vaporization of Zn.

TABLE 1

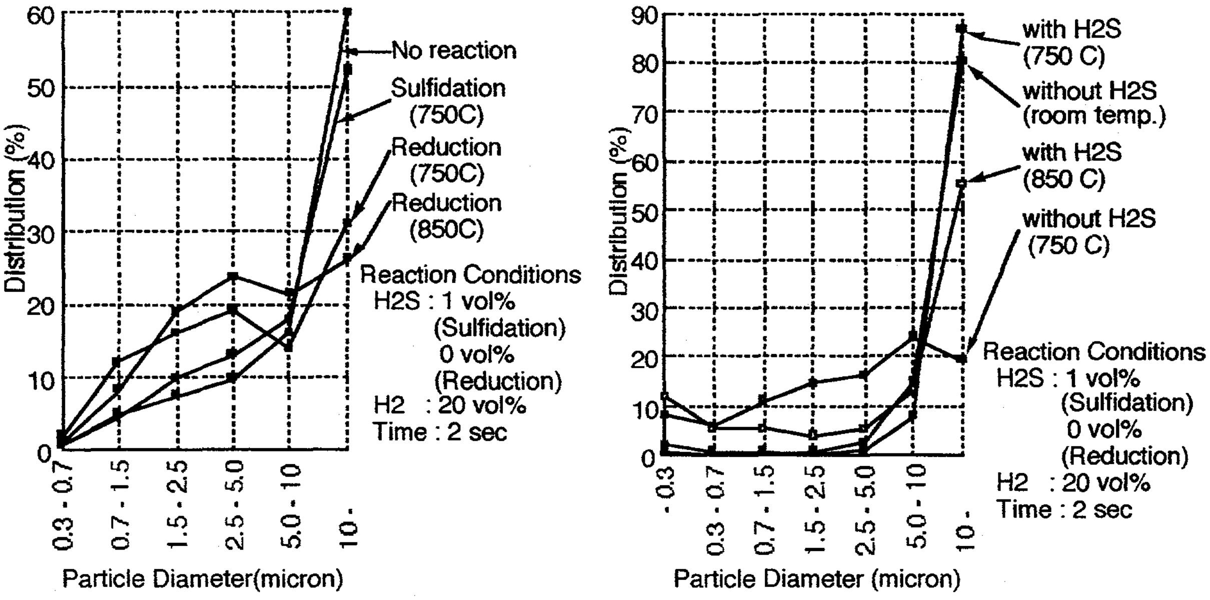
Reaction conditions for the drop-tube furnace experiments

Sorbent Size :	0.3 - 0.6 μm (pneumatic sieving) 30 - 63 μm (dry sieving)
Temperature :	620 - 850 °C
Reaction Zone Length :	5 - 30 cm
Bulk Flow Velocity:	5 - 10 cm/s (Reactant gas flow)
Jet Flow Velocity :	48 - 97 cm/s (The flow containing the sorbent)
Molar Composition :	H_2S; 0(reduction), 0.4 - 2.0 %
of reactant gas	H_2; 0 - 66 %, CO_2; 0 - 18 %
Carrier (Jet) Gas :	He, CO2, 6% H_2S - N_2, H_2

RESULTS

Reduction/sulfidation of ZnO sorbents

Fig. 4(a) shows size distributions of ZnO-2 sorbent measured with the cascade impactor after reduction/sulfidation reaction at various conditions. It is clear that the powder over 10 μm size decreased while the 1.5-5 μm size range increased after reduction. This suggests that formation and vaporization of elemental zinc take place in reduction. With H_2S in the reactant gas, however, the change of size distribution is small or negligible except at 850°C.



(a) Size distribution of sulfided/reduced ZnO-2 sorbent (b) Size distribution of sulfided/reduced metallic Zn

Fig. 4 Size distributions of ZnO-2 sorbent and metallic Zn powder after reduction/sulfidation reaction

In the sulfidation conversion measurement by in the TGA, no weight reduction associated with the vaporization of elemental Zn during the heating in N_2 was observed. This indicates that if any elemental Zn was deposited on the particles, it was quickly either sulfided by H_2S or oxidized by product water. This result coincides with a previous study that H_2S suppressed the reduction of ZnO [2]. The mechanism of decreased fines formation with H_2S may be the suppression of the reduction reaction itself or immediate sulfidation of Zn vapor formed. In order to examine the latter effect of H_2S separately, fine powder of metallic Zn was fed into the reactor with and without H_2S and its particle size distribution at the outlet of the reactor was measured. Fig. 4(b) shows the results a)without H_2S at room temperature (i.e. no reaction or vaporization), b)without H_2S at 750° C (i.e. no reaction but vaporization), c)with 1 vol% H_2S at 750°C, d)with 1 vol% H_2S at 850°C. This result shows that the existence of no more than 1 vol% of H_2S inhibited the vaporization of Zn almost completely at 750°C. At 850°C,however, the vaporization of Zn was so rapid that some of the vaporized Zn escapes the original particle surface to form fine powder of ZnS by gaseous sulfidation with H_2S.

Judging from the fact that the vaporization of metallic Zn was effectively suppressed by H_2S even with metallic zinc powder as the starting material, H_2S seems to suppress mainly the vaporization by immediate formation of ZnS, not the reduction reaction itself.

Assuming that the surface reaction is the rate limiting step and that other factors, such as gas composition gradient and particle velocity, are not influenced by temperature, the activation energy was calculated as 7.1 - 10.9 kcal/mol, slightly different depending on particle size. The particle size dependence of the sulfidation conversion was found to correspond to the particle surface area. This is because the conversion in almost all the experiments was no higher than 15%. In these tests, we could not exceed conversions higher than 15%.

Comparison of Sorbents

Table 2 shows the sulfidation conversions of ZnO-2(MIT), ZnO(Johnson Matthey), $ZnTiO_3$(Pfaltz & Bauer), and L-3140(UCI) sorbents at the same reaction conditions.

The difference between two types of ZnO mainly depends on the surface area because the surface reaction rates per surface area for are almost the same. The difference between ZnO-2 and zinc titanate depends on both the surface area and the lower reactivity of titanate[3]. The original particle size of L-3140 had little effect on sulfidation conversion or even on the observed size distribution in the cascade impactor, apparently due to agglomeration of fine particles.

TABLE 2

Sulfidation Conversions of ZnO and Zinc Titanate Sorbents

Sorbent	Initial Particle Size (μm)	Carrier Gas	Conversion (%)	Surface Reaction Rate (mol/cm2s)
ZnO-2(MIT)	40-52	H2	5.2	1.60E-8
		He	2.1	0.65E-8
ZnO (Johnson Matthey)	40-52	H2	0.6	1.84E-8
$ZnTiO_3$ (Pfaltz & Bauer)	40-52	H2	1.6	0.70E-8
L-3140(UCI)	40-52	He	6.9	2.37E-7
L-3140(UCI)	2.8-5.9	He	5.6	1.15E-8

Reaction conditions : 750°C, H_2S 1.0 vol%, H_2 20 vol%, Contact time = 2sec at reaction temperature
Diameter of analysed particle : 5-10μm

CONCLUSIONS

1) At 750°C or lower temperature, H_2S was found to almost completely inhibit the size decrease of sorbent particles caused by vaporization of elemental Zn formed by reduction of ZnO with H_2. This effect seems to be mainly suppression of zinc vaporization, not the reduction reaction.
2) At 850°C, fine particles less than 0.3 μm in diameter were formed even in the presence of H_2S. These fine particles were found to be ZnS formed by the reaction of vaporized zinc and H_2S and would be possibly captured by micro filtration. Therefore, at this temperature, vaporization of zinc and formation of fine particles aids the conversion of the sorbent.
3) ZnO sorbent has high potential for the sorbent injection hot gas cleanup process because ZnO has higher sulfur loading capacity and its drawbacks can be covered by the process.

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