

THE USE OF ZINC OXIDE SORBENTS TO REMOVE HYDROGEN SULFIDE  
FROM COAL GASES

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It is anticipated in the future that synthetic fuels derived from coal will be needed to replace the limited resources of petroleum and natural gas. Coal gasification is a necessary step in the production of these synthetic fuels. During coal gasification hydrogen sulfide is produced in oxygen deficient systems due to the sulfur compounds present in coal. In order to be able to use coal gas in molten carbonate fuel cells (MCFC) for electric power generation, hydrogen sulfide needs to be removed down to 1 ppm level. Therefore, it is very important to develop some sorbents to remove  $H_2S$  from a few percent down to 1 ppm level at high temperatures (600 to 650°C) to obtain greater process efficiency.

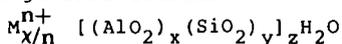
Several metal oxides are capable of high temperature sulfur removal (Westmoreland and Harrison, 1976). Iron oxide is one of the metal oxides that has been used to desulfurize coke oven gases. However, thermodynamic limitations does not allow  $H_2S$  removal with iron oxide to the low partial pressures necessary for MCFC operation. But it can be done with zinc oxide. Therefore, metal oxide-based sorbents for high temperature  $H_2S$  removal has been an active research area in recent years.

There has been much study concerning reactions between zinc oxide (ZnO) and hydrogen sulfide ( $H_2S$ ). Westmoreland and Harrison (1976) has reported the results of thermodynamic screening of the high-temperature desulfurization potential of 28 metal oxides by use of the free energy minimization method. According to the results of this study ZnO is among the most favorable oxides because of the high equilibrium constant for the ZnO- $H_2S$  reaction. In 1977 Westmoreland and Harrison published the results of a comparative study of the kinetics of high-temperature reactions between  $H_2S$  and selected metal oxides. The relative magnitude of the reaction rates determined was  $MnO > ZnO = CaO > V_2O_5$ . The major reasons that ZnO is a desirable sorbent are its high reactivity, high equilibrium constant for the ZnO -  $H_2S$  reaction and ability of ZnS to be regenerated (Rao and Kumar, 1981).

Results regarding structural changes in the pure ZnO sorbent at high temperatures are reported in the literature (Ranade and Harrison, 1980). Sintering actually causes the particles to shrink radially, thus with the same mass of particles there is a smaller amount of surface available for reaction.

The solution to this problem can be proposed by supporting the zinc oxide on a support which can stand to high temperatures. Such a support can be zeolites. Thus, more reaction surface area will be available for the reactant and sorbent efficiency can be increased.

Information about zeolites is given by Maxwell (1982). Zeolites are crystalline aluminosilicates with a chemical composition of this general formula:



$M_x^{n+}$  is the cation that balances the negative charge of the framework ions,  $Si_4^{+}$  and  $Al_3^{+}$ . The framework ions are tetrahedrally coordinated to four oxygen anions. The three-dimensional network is formed by linking  $(SiO_4)$  and  $(AlO_4)^-$  tetrahedra through shared oxygen ions. The tetrahedra form rings which are entrances to channels or cages in zeolites. The cages define the pore diameter of the zeolite particle. The drawing below shows the structure of the mordenite, Z type zeolite, which has been used for this study. In general, zeolites have good thermal stability, and the framework cations, usually sodium can be exchanged for different types of cations, including zinc. The mordenite type of zeolite is silica rich; therefore its hydrothermal stability is great (stability increases with decreasing aluminum content). This stability made the mordenite the obvious choice for this study. Zeolites seem to be a good way to combat the loss of surface area of the ZnO, due to sintering, because the zeolite support will be thermally stable during the ZnO-H<sub>2</sub>S reaction.

The objective for this paper is to determine if using zeolite supports for the zinc oxide-based sorbents improves conversion, making zinc oxide supported on zeolites a more efficient sorbent. Experimentally, the reactivity of zinc oxide-zeolite particles will be investigated, and kinetic data will be determined for the reaction. The results will then be compared with data found in the literature.

#### EXPERIMENTAL

The reaction of H<sub>2</sub>S with ZnO on zeolite support, whose mean diameter was 0.442 mm, was studied in the temperature range of 500 to 700°C. A plug-flow reactor was used which was 52 cm long and had an inside diameter of 2.2 cm. Figure 2 shows the schematic diagram of the reactor system. The total gas flow rate was held at high rate (1200 cm<sup>3</sup>/min) to eliminate the effect of external mass transfer for the gas solid reaction. The simulated gas mixture consisted of 4% H<sub>2</sub>S, H<sub>2</sub> and the rest N<sub>2</sub>. Gas analyses for each run were checked by taking samples from the sample port indicated in Figure 2 and injecting into the Gas Chromatograph.

Sorbent particles were prepared by soaking zeolite support particles in concentrated zinc sulfate solution, then drying them

about an hour at 100°C and finally roasting them for 24 hours at 500-600°C.

After zeolite particles were prepared, a sample of them was used to test for the determination of zinc loading on the particles. This test is performed by dissolving the zinc on the zeolite support in concentrated hydrochloric acid and determining the zinc content of the solution by atomic absorption spectrophotometer.

The reaction,  $H_2S + ZnO \rightarrow ZnS + H_2O$  was performed in the reactor. The reactor temperature was varied in a range of 500-700°C and gas samples were taken every 2 minutes during the reaction and analyzed by GC. After the reaction is completed, the feed gas was cut off and reactor was cooled down to room temperature with  $N_2$  gas. Finally, the samples were removed and analyzed to determine the extent of conversion of ZnO to ZnS.

The solubilization of ZnO and ZnS were different at different acidity solutions. By making use of this difference ZnO and ZnS were dissolved in solutions having different acidity and the zinc content of these solutions were determined by Atomic Absorption Spectrophotometer. Using the concentration of zinc in each solution, the conversion of ZnO to ZnS was found. A zinc balance was done for the samples to make sure that the amount of zinc (in ZnO and ZnS form) in the particles after the reaction was equal to the total amount of zinc in the particles before the reaction. This balance was met within +2%.

## RESULTS AND DISCUSSIONS

The results obtained from this experimentation are presented in Figures 3 and 4. Figure 3 represents the overall solid conversion of ZnO to ZnS with respect to time for the particle size under study at 500°C, 600°C and 700°C. As can be observed from the figure, the overall solid conversion depends on temperature and reaction time. The overall solid conversion increases as the temperature and reaction time increases. The conversion reaches to 100% at 500°C in about a total reaction time of 40 minutes. The total reaction times for 100% conversion at 600°C and 700°C are about 30 and 10 minutes, respectively. The reaction temperature above 700°C is not tested, because of the formation of metallic zinc vapor above 750°C. The maximum temperature in the ZnO- $H_2S$  system is limited to about 750°C thermodynamically (Westmoreland and Harrison, 1976). Experimental results have also been reported about this temperature at somewhat higher values by Beveridge (1962). During the tests hydrogen has been added to the feed gas mixture in a ratio of 3 mol  $H_2$ /mole of  $H_2S$  to prevent the decomposition of  $H_2S$  at high temperatures. It has been shown by Westmoreland and Harrison (1977) that the  $H_2$  does not measurably alter the  $H_2S$ -ZnO kinetics at low temperatures (<500°C) where  $H_2S$  decomposition should be unimportant.

One of the important reasons to support ZnO on zeolite in this study was to provide better contact between H<sub>2</sub>S and ZnO through increasing the surface area. The other reason was to minimize the structural changes of the ZnO particles during reaction due to sintering effects. Ranade and Harrison (1980) have found in their study of ZnO-H<sub>2</sub>S reaction that surface area of pure ZnO particles decreases from 34 m<sup>2</sup>/g to 16 m<sup>2</sup>/g at 500°C (a 53% decrease in the surface area). This change is more severe at higher temperatures. Since the molar volumes of ZnO and ZnS are not very different, pore plugging could not be a problem during the reaction. Therefore, they have attributed this decrease in surface area to sintering effects which causes the particles to shrink under the effect of high temperatures, thus decreasing the available surface area for the reaction considerably.

The answer to the question "Did structural changes occur in the ZnO-zeolite particles due to reaction?" was important in this study. The BET surface area measurements on the particles before and after reaction were performed using the Accusorb apparatus (Micromeritics Model 2100E).

Table I lists the surface area of reacted and unreacted particles for the longest reaction times for each reaction temperature. The BET surface area of (an average of five batches) unreacted ZnO-zeolite particles is 31.8 m<sup>2</sup>/g. The corresponding surface areas for particles reacted at 500° and 600°C for 50 minutes are 28.2 and 28.1 m<sup>2</sup>/g, respectively. The change is only 11% for these temperatures. At 700°C, the change becomes a little higher, being 15%. These changes in surface area are small as compared to 53% change reported by Ranade and Harrison (1981) at 500°C. Zeolite support is not expected to sinter. It is thermally stable. Therefore, the change in surface area could be attributed to partial sintering of ZnO with zeolite, especially around 700°C. However, some in-depth surface studies are needed to answer this question correctly.

A direct comparison of the conversion versus time curves with the data obtained from literature could not be done, because of the vast difference in the systems. Ranade and Harrison (1980) have investigated the H<sub>2</sub>S absorption with pure ZnO pellets, however our study uses ZnO supported on zeolite. Also, particle size, shape, zinc content will make the difference in comparison. Practically no information is available in the literature on the use of zinc oxide on a carrier or support to absorb hydrogen sulfide from hot coal gases.

Kinetic constants have been calculated for the reaction between H<sub>2</sub>S and ZnO. Zeolite particles using experimental data. The rate constant has been found to obey the Arrhenius relationship.

$$k = A \exp (-E/RT)$$

The Arrhenius plot is shown on Figure 4. A least squares linear fit has been used for the data points to find the slope and the intercept. The correlation coefficient is 0.929. The frequency factor, A, has been found to be  $1.781 \text{ cm}^2/\text{min-mol}$  and the activation energy, E, has been found to be 4355.5 calories/mol. The activation energy is small. Normally, such a low value would indicate mass transfer limitations. This is expected in this system, because of use of zeolites as support for ZnO. Usually zeolites have small pores. The diffusion resistance in zeolites is high. Also, high temperature gas-solid reactions tend to be diffusion controlled. However, this is the first trial on this concept of using support material for metal oxides to increase the surface area available for reaction. Also, authors wanted to test if zeolite had any effect by itself on H<sub>2</sub>S absorption. A base experiment has been conducted using plain zeolites (no ZnO deposits). No decrease in H<sub>2</sub>S concentration has been observed with time.

#### CONCLUSIONS

Using zeolite as support material for zinc oxide does not seem to be suitable. A higher porosity and larger pores are desirable for this kind of application. Nevertheless, the results of this study showed that sintering of sorbent particles can be minimized or prevented by using this new concept of depositing metal oxides on thermally stable supports. Further research on this subject is in progress.

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TABLE I. BET SURFACE AREAS FOR MAXIMUM REACTION TIME  
(TIME = 50 MINUTES)

SAMPLE	SURFACE AREA ( $m^2/g$ )
*****	*****
RUN NO. 5 T=500 C	28.2
RUN NO. 10 T=600 C	28.1
RUN NO. 11 T=700 C	26.9
UNREACTED ZnO-ZEOLITE PARTICLES	31.8

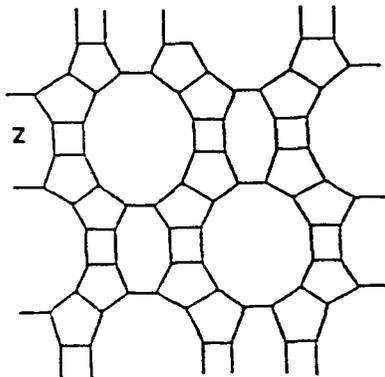


FIGURE 1. SCHEMATIC DIAGRAM OF A Z TYPE ZEOLITE

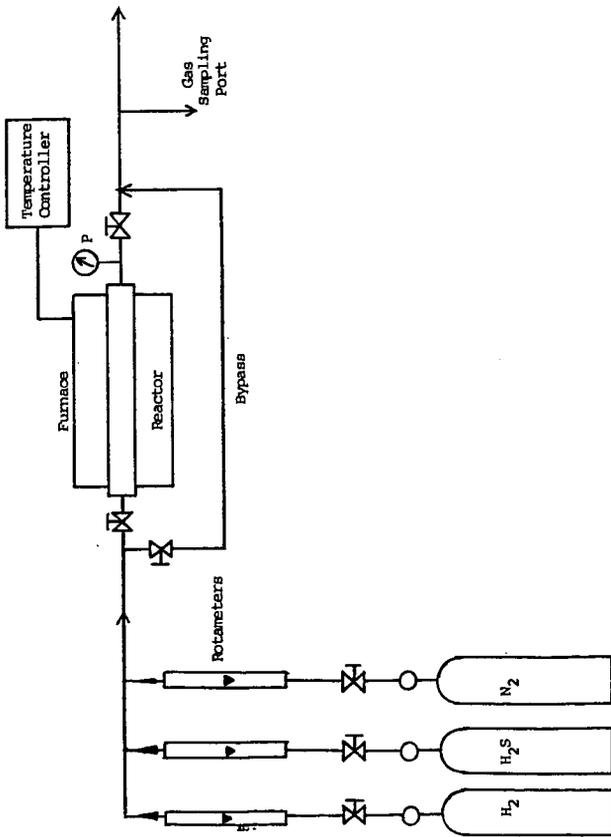


Figure 2. Schematic diagram of laboratory set up for kinetic studies.

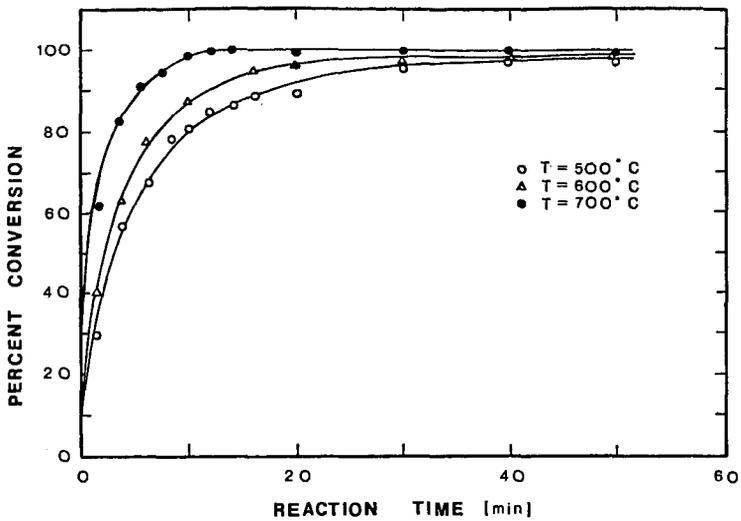


Figure 3. Conversion with reaction time, ZnO - H<sub>2</sub>S reaction.

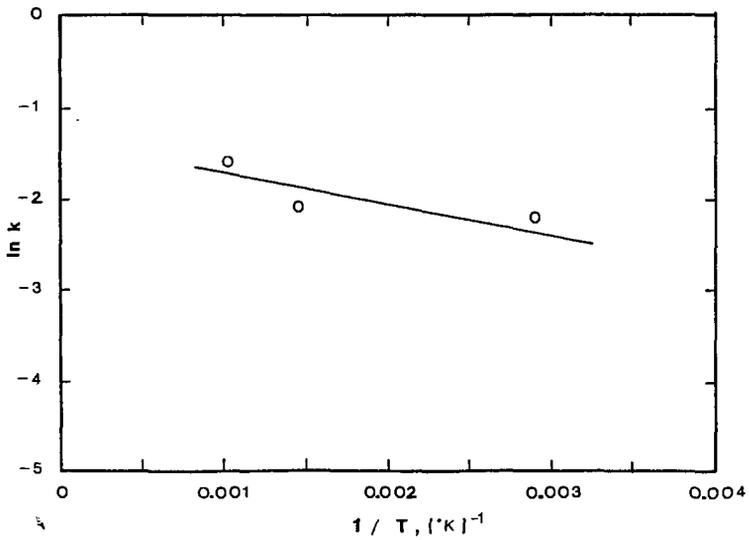


Figure 4. Arrhenius plot ZnO - H<sub>2</sub>O reaction.