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Low-Temperature H₂S Removal from Steam-Containing Gas Mixtures with ZnO for Fuel Cell Application. 1. ZnO Particles and Extrudates

Ivan I. Novochinskii,[†] Chunshan Song,^{*,†} Xiaoliang Ma,[†] Xinsheng Liu,[‡]
Lawrence Shore,[‡] Jordan Lampert,[‡] and Robert J. Farrauto[‡]

*Clean Fuels and Catalysis Program, The Energy Institute and the Department of Energy and
Geo-Environmental Engineering, Pennsylvania State University, 209 Academic Projects
Building, University Park, Pennsylvania 16802, and Corporate Research Center,
Engelhard Corporation, 101 Wood Avenue, Iselin, New Jersey 08830*

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Sulfur removal is important for a fuel cell that uses a hydrocarbon fuel, such as natural gas, liquefied petroleum gas, and gasoline, to prevent the downstream sulfur poisoning of catalysts in the fuel processor and in the fuel cell anode. Although most sulfur species are removed prior to reforming, the reducing environment of the reforming stage (such as autothermal reforming) converts residual sulfur to hydrogen sulfide (H₂S). H₂S in the reformat must be removed to ensure longevity of the catalysts in downstream processing and in the anode chamber of fuel cell systems. A unique modified ZnO sample with a different morphology has been prepared and comparatively studied together with a commercially available ZnO sample under various conditions. Extremely low H₂S outlet concentrations—as low as 20 parts per billion by volume (ppbv)—have been observed over the modified ZnO sample for extended periods of times. The sulfur-trap capacity (the amount of H₂S trapped before breakthrough) also is dependent on space velocity, temperature, steam concentration, CO₂ concentration, and particle size. Higher capacity is observed at higher H₂S inlet concentration of 8 ppmv, compared to lower inlet concentrations of 1–4 ppmv. The trap capacity decreases monotonically as the temperature increases. Steam in the reformat inhibits the capture of H₂S by ZnO; it seems to shift the equilibrium of the reaction $\text{ZnO(s)} + \text{H}_2\text{S(g)} \rightleftharpoons \text{ZnS(s)} + \text{H}_2\text{O(g)}$ to the left, toward ZnO and H₂S. The effect of steam seems to be reversible. Increasing the CO₂ concentration in the feed up to 12 vol % decreases the capacity of ZnO for the capture of H₂S.

Introduction

In the past decade, the integrated gasification combined cycle (IGCC) and fuel cells (FCs) have been considered to be among the most-promising processes for advanced electric power generation. These emerging technologies will not only significantly improve the thermal efficiency but also will reduce or eliminate the environmentally harmful pollutants that are associated with the combustion of fossil fuels. Usually, after gasification of the fuels, sulfur exists as hydrogen sulfide (H₂S). The deep removal of H₂S from gasified fuel gases is a significant concern that stems from (i) the stringent environmental regulations, (ii) the need to prevent poisoning the catalysts downstream, (iii) the need to protect turbines from corrosion, and (iv) the need to protect the FC anode catalyst and also the fuel-processing catalyst in a proton exchange membrane (PEM) FC system that uses a hydrocarbon fuel. That is why an increasing amount of attention has been focused on the development of various materials and methods for sulfur removal for either IGCC or FC applications.

Westmoreland and Harrison¹ and Hepworth et al.² performed comparative studies on different absorbent systems that consisted almost entirely of different metal oxides. These studies can be divided into two groups, with respect to the operating temperatures: high temperature, >600 °C (Ba, Ca, Sr, Cu, Mn, Mo, W); and low temperature, 300–550 °C (V, Zn, Co, Fe).

Candidate absorbents should meet several requirements to be considered for commercial gas desulfurization. The most important feature is that it should be theoretically capable of decreasing gas-phase sulfur concentrations to the low levels required by downstream processes (below 0.1 parts per million by volume (ppmv) for PEM FC and below 20 ppmv for IGCC) under the relevant conditions. In addition, the absorbent must have acceptable sulfur capacity (in terms of both theoretical value and achievable range), preferably be regenerable, and maintain activity and capacity through a large number of sulfidation/regeneration cycles. The absorbent should also be nonpyrophoric for FC applications.³ Finally, the cost of the absorbent must be reasonable.

Not much attention has been given to the desulfurization of steam-containing gas mixtures with low H₂S

* Author to whom correspondence should be addressed. E-mail address: csong@psu.edu.

[†] Pennsylvania State University.

[‡] Engelhard Corporation.

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(2) Hepworth, M. T.; Ben-Slimane, R.; Zhjeng, S. *Energy Fuels* **1993**, *7*, 602–609.

concentration (<10 ppmv) at 300–400 °C, which is the so-called low-temperature range, because it is much lower than those (600–850 °C) widely used for desulfurization of gases from coal gasification. There are several applications where an extremely low (<1 ppmv) sulfur concentration is required. They include the catalytic water-gas shift process, ammonia synthesis, the use of hydrogen-rich gas as the feed for a PEM fuel cell using reformat gas from hydrocarbons, and pure hydrogen for chemical applications. Low-temperature H₂S absorption is efficient on hydrated iron oxide; however, it has been replaced by zinc oxide (ZnO)^{4,5} for environmental and safety reasons. ZnO is a promising material, because it can provide a desirable level of H₂S removal.^{6,7} What is also very important is that ZnO is nonpyrophoric, even after use in a reducing atmosphere at 350–450 °C. Manganese oxide (MnO) also is stable in a reducing atmosphere at 400 °C. The main drawback of manganese-based absorbents is higher outlet H₂S concentrations. The fuel gas that contains 5% H₂O and 1% H₂S (10 000 ppmv) can be desulfurized at 727 °C to 57 ppmv H₂S with MnO and to 6 ppmv H₂S with ZnO.⁸

ZnO has been widely used for more than 30 years as a H₂S removal agent from natural gas.⁹ The achieved dynamic capacity was 22–24 wt % (370 °C, 400 h⁻¹), with a maximum-possible sulfur loading of 33%, which corresponds to the complete conversion of ZnO to ZnS. If the amount of sulfur in the feed gas concentration is very small, then on-site regeneration is not necessary for some applications. For such cases, upon breakthrough, the absorbent bed is replaced with a fresh batch of ZnO and then sulfur removal continues. From this point of view, the use of ZnO as a polishing bed is desirable. Therefore, ZnO is an unique oxide that can respond to many requirements of processing and safety. The main challenge for using ZnO as a polishing bed for FC applications is that it must be effective in preventing gases from reforming as hydrocarbons in H₂ + CO + H₂O + CO₂ mixtures. The gas that originates from the steam reformer or autothermal reformer contains a high steam concentration (up to 35 vol %) and low H₂S concentration (~1–2 ppmv in the case of natural gas).

The present study is devoted to the behavior of ZnO-based absorbents for H₂S removal related to hydrocarbon fuel reforming for FC applications, with an emphasis on the influence of the type of ZnO material, and reaction conditions (inlet H₂S concentrations, steam concentration, temperature, space velocity (SV), etc.) on its capacity in the low-temperature range (300–400 °C).

Experimental Section

Commercially available ZnO samples (HTZ-5, supplied by Haldor–Topsoe) and ZnO samples prepared by Engelhard

Corporation (58% of which was pure ZnO, with a Ca-bentonite binder comprising the reminder) were tested. ZnO-based samples were supplied in the form of 3-mm cylinder extrudates. The ZnO extrudate sample from Haldor–Topsoe was prepared using commercially available ZnO powder, and the extrudates were made without any binder or additives, according to the sample specification. For the samples from Engelhard, commercially available ZnO powder was chemically modified via a pretreatment procedure, mixed with a binder, and then extruded. The pretreatment procedure is described as follows: 12 g of ZnO were placed in 40 mL of saturated water solution of (NH₄)₂CO₃, and the slurry was stirred with a magnetic stirrer for 2 h. In a separate vessel, 8 g of a binder (Ca-bentonite) was calcined at 200 °C for 2 h in air. The calcined binder was added to the slurry and mixed thoroughly. The extrudate was prepared using the mixture with a standard extrusion machine, followed by drying at 120 °C for 2 h in air and calcination at 300 °C for 2 h in air.

The modified ZnO powders (without binder) that were used in the preparation of the extrudates by Engelhard were also used for the kinetic study in this work. The bulk chemical composition of the ZnO powder samples (without binder) from both Engelhard and Haldor–Topsoe is ZnO; however, these samples differ in morphology and surface area (see below).

A fixed-bed flow reactor was fabricated in our laboratory at Pennsylvania State University and coupled with an on-line H₂S analyzer (Figure 1). Special tubing and fittings coated with a Sulfinert material (purchased from Restek Corp.) were used for the reactor construction. The reactor tube was made of Pyrex glass with an inner diameter of 10 mm, unless otherwise mentioned. The ZnO samples were packed in the tube, with sample sizes ranging from 0.917 g in the case of particles to 4 g in the case of 3-mm extrudates, depending on the need to examine the effect of operating conditions and to determine the capacity. The loadings of 3-mm extrudates were 4 g in all cases. The total height of the packed bed was 32 mm in all experiments with extrudates. The ratio of bed height to bed diameter was ~3. The ratio of sample bed height to extrudate diameter was ~10. The absorbent bed was maintained essentially isothermal, and the temperatures in both the top and bottom of the absorbent bed were monitored. Feed gas contained 1–8 ppmv H₂S, 43% H₂, with the balance being nitrogen (N₂), to which water vapor was added from the top of the bed. All the gas flow rates were controlled with mass-flow controllers supplied by Brooks Instruments (model 5850E, with an accuracy of ±1% of full scale). The gas flow rate, on a dry basis, was 200–500 mL/min. When the dry gas flow rate was 200 mL/min, a H₂O addition of 15% means 200 mL/min + 30 mL/min of steam, for a total flow rate 230 mL/min, where the H₂ concentration was 37% and the H₂O concentration in the resulting mixture was 13%. When 25% steam (50 mL/min) was added to the dry gas flow (200 mL/min), the concentration of H₂O in the resulting gas flow (250 mL/min) mixture was 20%.

The outlet H₂S concentration was monitored using an ONIX CVI H₂S analyzer (supplied by Thermo ONIX) with measurement ranges of 0–100 ppbv and 0–10 ppmv full scale, with an error of ±2% of full scale. Full scale was 0–1000 ppbv in all our experiments. The H₂S sample flowed to the bubbler humidifier, which contained a bubbler solution (5% acetic acid in deionized water). After exiting the bubbler humidifier, the sample flowed into the tape deck chamber, where it reacted with a segment of the sensing tape. H₂S concentration in the sample is determined by the rate of color change of the tape, which is produced by the chemical reaction between the H₂S and the lead acetate-impregnated sensing tape.

Calibration of the sulfur analyzer was performed carefully in the low-H₂S-concentration range, using a certified gas mixture (10 ppmv H₂S in ultrahigh-purity nitrogen). H₂S and N₂ were dosed with the help of mass-flow controllers (model 5850E, Brooks Instruments). The calibration curve is shown

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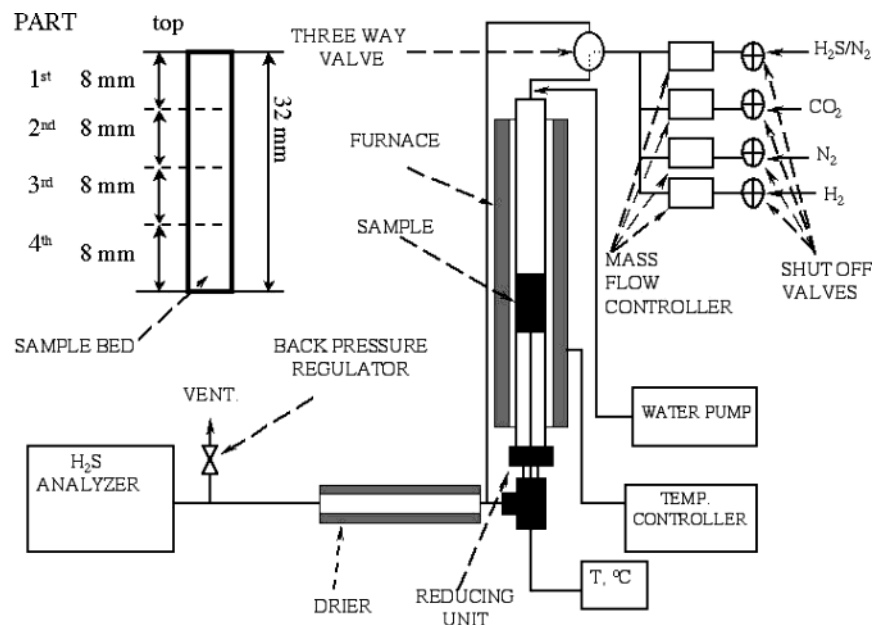


Figure 1. Scheme of the fixed-bed reactor for H_2S capture. Inset in the upper left-hand corner shows the bed of absorbent sample and how the used sample from the bed was divided for analysis.

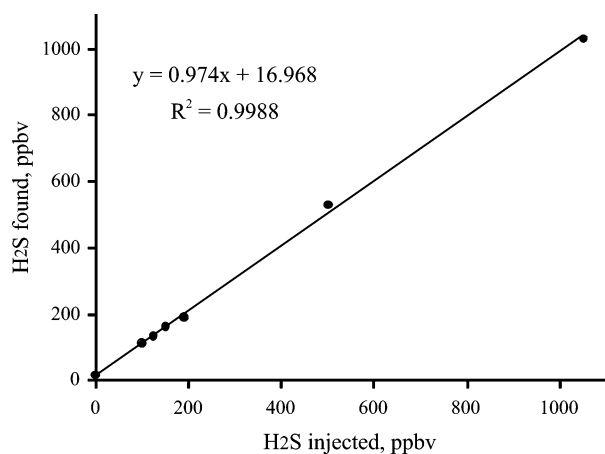


Figure 2. Calibration results for H_2S analysis in the range of 0–1000 ppbv. The instrument (ONIX CVI H_2S analyzer) was calibrated using up to 1000 ppbv H_2S in a gas mixture with N_2 .

at the Figure 2. The value of 100 ppbv was accepted as the reliably measured H_2S concentration.

The capacity (grams of sulfur per 100 g of sample, g S/100 g sample) of the samples was calculated using the following formula:

$$S_{\text{cap}} = \frac{\text{BT} \times \text{FR} \times C_{\text{H}_2\text{S}} \times 32 \times (6 \times 10^{-4})}{V_{\text{mol}} m_{\text{sample}}}$$

where S_{cap} is the sulfur capacity (in units of g S/100 g sample) and BT is the breakthrough time (in hours). The breakthrough time is the time when H_2S concentration in outlet flow reaches 100 ppbv (Figure 3); FR is the flow rate (in units of L/min), $C_{\text{H}_2\text{S}}$ is the H_2S concentration (in units of ppmv), 32 g/mol refers to the molar weight of sulfur, V_{mol} is the molar volume (24.45 L/mol, under standard conditions), m_{sample} is the sample weight (in grams), and 6×10^{-4} is the normalizing coefficient, adjusting the units.

The fresh and used ZnO samples were analyzed for pore volume and pore-size distribution. Mercury porosimetry of the ZnO samples was performed using a PoreMaster 60 GT instrument (manufactured by Quantachrome Instruments).

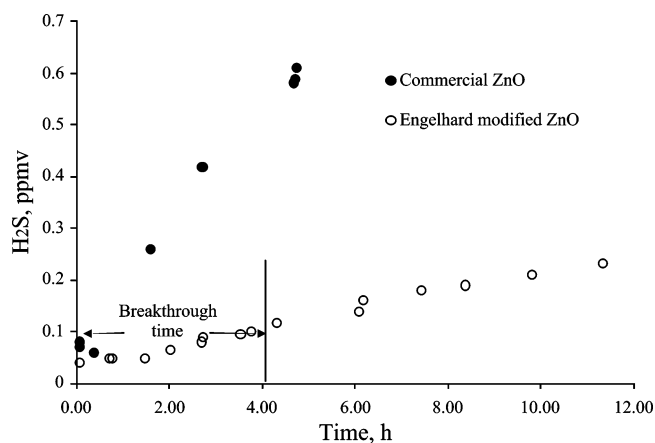


Figure 3. Typical H_2S outlet concentration profile for 3-mm extrudates of commercial ZnO sample and a modified ZnO-based absorbent newly developed at Engelhard (400 °C, space velocity (SV) of 8775 h^{-1} , 8 ppmv H_2S , 37% H_2 , 20% H_2O , with the balance being N_2 ; using a Pyrex reactor with an inner diameter of 20 mm).

Results and Discussion

Figure 3 shows the profiles for H_2S removal, using a commercially available ZnO and the modified ZnO-based absorbent from Engelhard at 400 °C (3-mm extrudates, with the following conditions: 8 ppmv H_2S , 37% H_2 , and 20% H_2O , with the balance being N_2 ; space velocity (SV) of 8775 h^{-1}). The ZnO extrudate sample from Engelhard, which was prepared using a special chemical modification (via ammonium carbonate pretreatment of ZnO), provides an extremely low H_2S outlet concentration (see Figure 3). The outlet H_2S concentration in the case of the commercially available ZnO immediately exceeds 0.1 ppmv. The outlet H_2S concentration in the case of modified ZnO absorbent was significantly less. Even after 20 h, it was only 0.3 ppmv.

Because the initial outlet concentration is very low, the performance of the Engelhard sample has been described through breakthrough time (BT), which is the time when the outlet H_2S concentration exceeds 0.1

Table 1. Comparison of ZnO-Based 3-mm Extrudates for H₂S Capture^a

particle size	capacity (g S/100 g ZnO)
3 mm, Engelhard ZnO extrudates	0.047
3 mm, commercial ZnO extrudates	≤0.012

^a Conditions are as follows: 400 °C; SV = 8776 h⁻¹; 8 ppmv H₂S, 34.4% H₂, and 20% H₂O, with the balance being N₂.

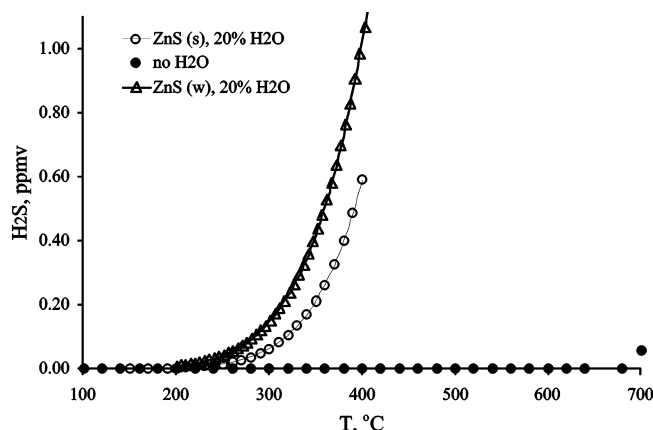


Figure 4. Calculated equilibrium H₂S concentration at different temperatures in the ZnO–ZnS–H₂O–H₂S system. The initial concentrations were as follows: H₂, 34.4%; H₂S, 8 ppmv; balance, N₂. Activity coefficients of all compounds were assumed to be equal to 1. “ZnS (s)” denotes a sphalerite structure, and “ZnS (w)” denotes a wurtzite structure.

ppmv. This value is also used to evaluate the dynamic capacity of sulfur capture before H₂S breakthrough. Calculation of the amount of H₂S trapped at the BT time gave the dynamic capacity shown in Table 1, which indicates that, in comparison, the capacity of the Engelhard ZnO sample is at least 3 times higher than that of the commercially available ZnO sample.

The equilibrium H₂S concentration for the system was calculated for the ZnO–ZnS–H₂O–H₂S system at 400 °C (Figure 4), which is ~0.6 ppmv for ZnS (sphalerite) and ~1 ppmv for ZnS (wurtzite). (The software system, HSC Chemistry, from Outokumpu Research Oy in Finland, was used to perform the thermodynamic equilibrium calculations, giving the results shown in Figure 4.) The two forms of ZnS give two equilibrium H₂S concentrations values that are very similar to each other. For both cases, there are major differences between the reactions with and without the presence of steam (H₂O). The reaction with dry gas can lead to complete H₂S capture by ZnO (forming ZnS) at equilibrium in a wide range of temperatures up to 650 °C. In the presence of 20% H₂O, however, H₂S breakthrough can easily occur at 200–400 °C. The activity of the solid used to calculate the results in Figure 4 is unity, as is common practice.

One may ask why the outlet H₂S concentration can be lower than the equilibrium H₂S concentration that is determined by the thermodynamic equilibrium calculations. The experiments were performed in a flow system that is not necessarily in equilibrium. At the very beginning of the reaction, the sample is not in equilibrium with the gas phase, because it does not contain ZnS. The reverse reaction would be very slow at the very beginning of the experiment. The newly formed ZnS species could be hardly described using the equation [$\Delta H = f(T)$; $\Delta S = f'(T)$] that is applicable to

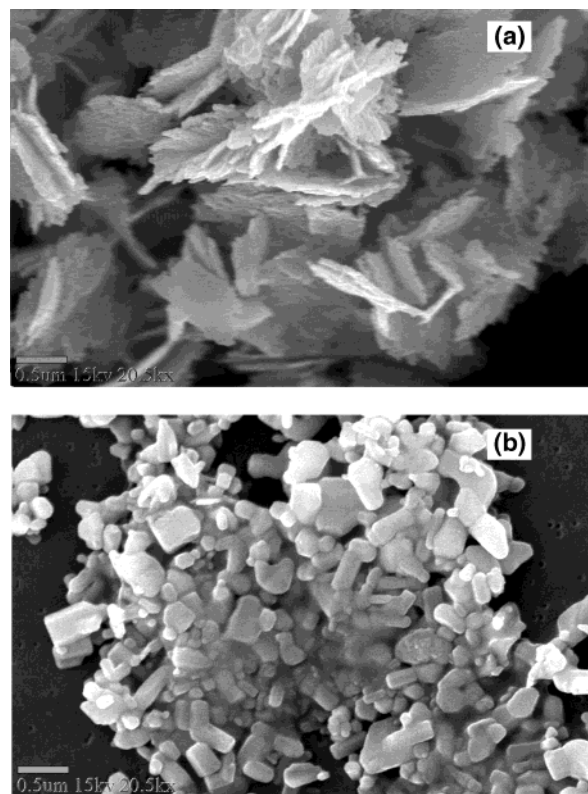


Figure 5. SEM micrographs showing the morphology of (a) a ZnO-based sample from Engelhard and (b) a commercially available ZnO-based sample.

the bulk phases. Because no ZnS is present in the fresh absorbent, the rate of the reverse reaction is much slower than the rate of the forward reaction in the initial stage. Thus, a lower H₂S outlet concentration would be observed initially, until a certain amount of ZnS is accumulated in the sample. The second contributing factor might be the deviations in real reactions from equilibrium calculations that assume that the activity coefficients of all the solid components are equal to 1 and all the vapor species are ideal gases. Note that the activity coefficients of the solid phases may have values that are smaller than unity. The activity coefficient values have an impact on the equilibrium H₂S concentration. In the real flow reactor, some of the reactant gases are not ideal under the reaction conditions. Other researchers have made similar observations that the measured H₂S concentrations are lower than the calculated equilibrium H₂S concentrations. For example, Pineda et al.¹⁰ reported the H₂S outlet concentration to be almost 5 ppmv (with the following feed gas composition: 1 vol % H₂S, 8 vol % H₂, 15 vol % CO, 15 vol % H₂O, with the balance being N₂; ZnTiO₃, 600 °C) when the calculated equilibrium concentration was 20 ppmv.

A question that arises concerning the ZnO materials is what causes the major difference in performance between commercially available (HTZ-5) and newly developed ZnO samples (as shown in Figure 3). On the basis of analytical characterization using scanning electron microscopy (SEM), this difference is largely due to their differences in ZnO crystal morphology, as can be seen from the SEM photographs shown in Figure 5.

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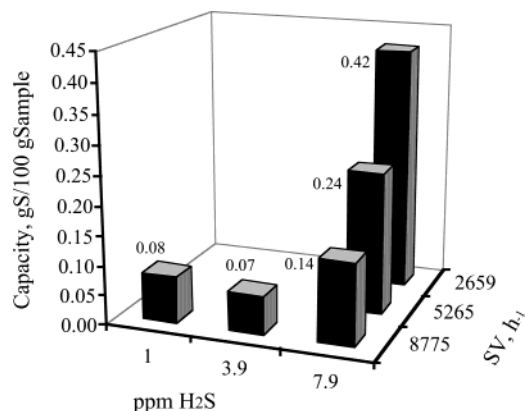


Figure 6. Influence of inlet H_2S concentration and space velocity (SV) on the capacity of 3-mm extrudates of ZnO absorbent from Engelhard at 300 °C, 34.4% H_2 , and 20% H_2O , with the balance being N_2 .

The ZnO sample from Engelhard displays a unique flake form, as compared to the form of aggregate particles in the commercially available ZnO sample. The H_2S removal reaction is a typical gas–solid reaction. External mass transfer or H_2S diffusion through the product layer (ZnS) might limit the reaction rate.^{3,11} In the case of flake or flat plates, the external mass-transfer limitations are much lower than those with cubes or prisms. The reaction should proceed faster and more effectively than in the case of cubes with low external (geometric) surface area, which leads to better performance of the absorbent. Therefore, the method used to prepare the modified ZnO sample is superior, in that it leads to a structure that facilitates gas diffusion and gas–solid reaction.

To determine the capacity of the modified Engelhard ZnO absorbent under different operating conditions, the samples were tested under different SV values and inlet H_2S sulfide concentrations. The results for using the 3-mm extrudates are summarized in Figure 6. The inlet H_2S concentration has a small influence on the sulfur capacity. Higher H_2S absorption capacity was obtained at a higher inlet H_2S concentration (8 ppmv), compared to the relatively lower H_2S inlet concentrations (1–4 ppmv). The SV value seems to have a major impact on H_2S capture capacity (see Figure 6). The higher capacities were observed at lower SV values. The dynamic capacity was 0.08 g S/100 g ZnO at 1 ppmv of inlet H_2S and 8775 h^{-1} and 0.14 g S/100 g ZnO at 8 ppmv of H_2S and 8775 h^{-1} . At 2659 h^{-1} and 8 ppmv of H_2S , the dynamic capacity was 0.42 g S/100 g ZnO. The observed trend highlights the fact that the performance of the ZnO-based trap can be influenced strongly by mass transfer between the bulk gas phase and a “clean” ZnO surface.^{3,11} Because the diffusion rate is first order, in regard to H_2S , H_2S penetration to the “clean” surface of ZnO would be faster at higher concentrations. Lower SV values allow more time for H_2S to reach the surface of ZnO that is uncovered with sulfide species.

The influence of ZnO particle size on the sulfur capacity was examined, and the results presented in Table 2 show that the reaction is more likely limited by diffusion. The maximum capacity is achieved with

Table 2. Effect of the Grain Size of ZnO Samples on H_2S Trap Capacity^a

particle size	capacity (g S/100 g ZnO)
3 mm, Engelhard ZnO extrudates	0.417
0.15–0.25 mm	2.70
0.106–0.15 mm	2.81
0.053–0.075 mm ^b	2.14

^a Conditions are as follows: 300 °C; SV = 2660 h^{-1} ; 8 ppmv H_2S , 34.4% H_2 , and 20% H_2O , with the balance being N_2 . ^b A significant decrease in pressure was observed.

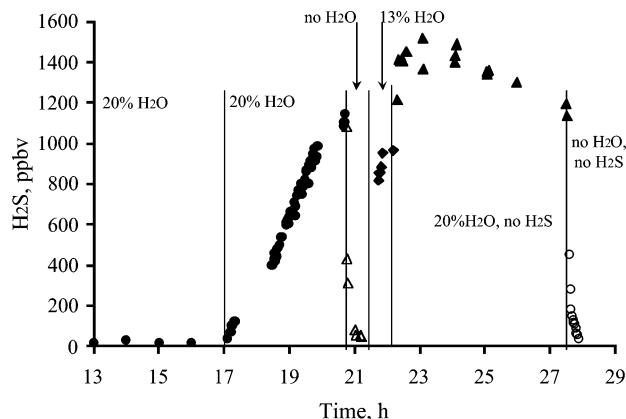


Figure 7. Performance of a ZnO-based trap at different concentrations of water vapor and H_2S . Absorbent was aged in a flow (with conditions of 1.2 ppmv H_2S , 34.4% H_2 , 20% H_2O , with the balance being N_2) for 17 h at 300 °C (shown partially as the first part of this figure). Subsequent testing was performed using a flow with the following conditions: 43% H_2 and prescribed concentrations of H_2O and H_2S , with the balance being N_2 at 400 °C. All the additives (H_2O and H_2S) are marked in the chart.

particles 0.106–0.15 mm in size. Further crushing to a smaller particle size (0.053–0.075 mm) did not improve the capacity. When the particle size was <0.1 mm, large decreases in pressure across the absorbent bed (over 1 atm) were observed. The pressure difference probably was responsible for the observed poor performance with the very small particles (0.053–0.075 mm). On the other hand, even after crushing 3-mm extrudates to particles 0.10–0.15 mm in size, the capacity of ZnO absorbent for H_2S capture from the steam-containing gas is still rather low (2.8 wt %).

Figure 7 shows the effects of steam concentration on H_2S removal using a ZnO-based trap with particles of ZnO plus binder 0.15–0.25 mm in size (from Engelhard). In this set of experiments, the H_2S removal was first conducted using the gas mixture that contained 1.2 ppmv H_2S and 20% of water at 300 °C for 17 h (the first region in Figure 7, up to 17 h). The temperature was then elevated to 400 °C. The reaction was conducted until the outlet H_2S concentration had reached that in the feed gas (the second region, from 17 h to ~21 h), which means that the capacity of the sample was completely used in the presence of 20 vol % H_2O and the absorbent could not take any more H_2S from the flow under the conditions used. However, when water flow valve was closed but the feed gas flow (with 1.2 ppmv H_2S) continued, the H_2S outlet concentration immediately decreased to a level of <20 ppbv (the third region in Figure 7). This means that the sulfur-capturing capacity of ZnO was recovered when steam was removed from the feed gas. At this point, the surface of ZnO can still absorb H_2S as long as water is absent. In

other words, water is inhibiting H₂S uptake on the surface of ZnO.

After the steam addition was stopped, the subsequent injection of 13% of water raised the outlet H₂S concentration to 1 ppmv (the fourth region, marked with 13% H₂O in Figure 7). In the presence of a smaller amount of water vapor in the flow, the sample was not saturated completely with H₂S and a small amount of H₂S was removed from the flow.

The final proof that water shifts the steady state was gained from the hydrolysis (reverse reaction) of the accumulated ZnS. If the gas feed contains no H₂S but has 20 vol % H₂O, then the formation of H₂S and its release into the outlet gas will be the evidence of the ZnS hydrolysis reaction. As shown in Figure 7 (the fifth region, between 22 and 27 h), after the addition of 20 vol % water vapor to the H₂/N₂ flow, which contains no H₂S in the feed gas, the outlet H₂S concentration reached a value of >1.2 ppmv.

In such a case, the concentration of "released" H₂S gradually decreased (Figure 7). The capacity of absorbent in the presence of 20% of water vapor was reached previously (because the H₂S breakthrough was noted already; see Figure 7). The subsequent tests with different vapor concentrations further accumulated ZnS in the absorbent bed. Under conditions where reaction of water with ZnS in the absorbent bed occurs, such reaction can re-produce H₂S. This is the reason the outlet H₂S concentration could exceed the 1.2 ppmv level (Figure 7) when the initial H₂S concentration in the feed gas mixture was only 1.2 ppmv.

The observed trends from the present work (Figure 7) clearly shows that a higher steam concentration inhibits H₂S capture and shifts equilibrium reaction (1) toward ZnO and H₂S; higher steam concentrations can also cause the hydrolysis of ZnS, which leads to the release of previously captured H₂S ($\text{ZnS(s)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{ZnO(s)} + \text{H}_2\text{S(g)}$), which is consistent with the thermodynamic analysis. It is possible that water could inhibit H₂S reaction with ZnO by a competitive adsorption on the ZnO surface, although Davidson and co-workers^{6,12} reported a positive role of small amounts of water formed in the reaction. H₂O might have a promoting role at very low steam concentrations, but the present study is concerned with the reformate from autothermal reforming and steam reforming for fuel cells, where the gas mixture contains a large amount of steam. It seems that the negative effects of H₂O on H₂S capture by ZnO can be attributed to the reverse reaction (hydrolysis of ZnS), and competitive adsorption, although the behavior of ZnO and ZnS in the presence of very low water concentration (e.g., <1%), is still unclear.

When water and H₂S flows were stopped but H₂-N₂ gas flow continued at 400 °C (the last region in Figure 7, up to 29 h), no H₂S was detected in the outlet gas. At this point, ZnS is still in the absorbent bed, and if hydrogen causes the decomposition or reduction of ZnS, then H₂S should be detected in the outlet flow. This observation seems contradictory to the proposal made in a study by Sasaoka,¹³ where hydrogen was proposed to decompose ZnS, forming Zn atoms and H₂S at 400

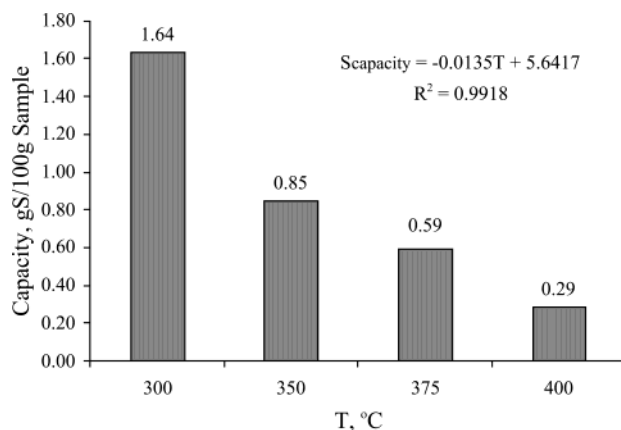


Figure 8. Capacity of a ZnO-based H₂S trap (absorbent grains 0.15–0.106 mm in size, from Engelhard) at different temperatures. Conditions were as follows: 2660 h⁻¹, 8 ppmv H₂S, 34.4% H₂, 20% H₂O, with the balance being N₂.

Table 3. Effect of Temperature on Capacity of ZnO-Based Absorbent^a

temp, T(°C)	Capacity	
	g S/100 g ZnO	g S/100 g sample
300	2.81	1.64
350	1.46	0.85
375	1.02	0.60
400	0.49	0.28

^a Conditions are as follows: 0.15–0.106 mm grains of sample from Engelhard containing binder; 2660 h⁻¹; 8 ppmv H₂S, 34.4% H₂, 20% H₂O, with the balance being N₂.

°C. On the other hand, a significant amount of ZnS was already hydrolyzed upon contact with gas that contained 20 vol % H₂O in a H₂-rich mixture without H₂S (region 5 in Figure 7); thus, the present experimental results cannot exclude the possibility that ZnS may be decomposed by hydrogen at 400 °C, especially in the presence of H₂O vapor.

Reaction temperature has a major impact on the performance of a ZnO-based absorbent. In the range of 300–400 °C, the capacity decreases monotonically as the temperature increases, as shown in Figure 8 and Table 3. The observed trend is in contrast with the results reported by Davidson,¹⁴ where higher conversions were observed at higher temperature, especially in the case of small grains (0.053–0.062 mm). The difference could be attributed to the difference in composition and preparation method of the absorbent. In our case, it was a binary mixture of ZnO and binder. A complex absorbent that contained ZnO, calcium oxide (CaO), magnesium oxide (MgO), and aluminum oxide (Al₂O₃) (calcined at 600 °C before use) was tested by Davidson.¹⁴ During high-temperature pretreatment, various types of new compounds (such as aluminates or zincates) might be formed. CaO was reported to decrease the conversion of ZnO to ZnS at room temperature.⁶ Calcium oxides and magnesium oxides are well-known absorbents of hydrogen sulfides in the temperature range of >700 °C.^{15,16} When the reaction temperature is increased to temperatures this high, calcium

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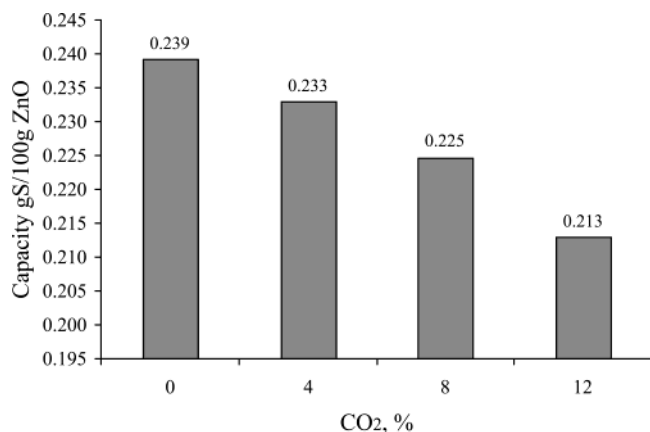


Figure 9. Dynamic capacity of a ZnO-based H₂S trap (3-mm extrudates) at different CO₂ concentrations. Conditions were as follows: 300 °C; SV = 8775 h⁻¹; 8 ppmv H₂S, 43% H₂, 4–12 vol % CO₂ (based on dry flow), with the balance being N₂; 20 vol % H₂O (based on wet flow).

Table 4. Influence of CO₂ Concentration on the Dynamic Capacity of 3-mm ZnO Extrudates from Engelhard^a

CO ₂ concentration (%)	capacity (g S/100 g ZnO)
0	0.239
4	0.233
8	0.225
12	0.213

^a Conditions were as follows: 300 °C; SV = 8775 h⁻¹; 8 ppmv H₂S, 43% H₂ and 0–12 vol % CO₂ (based on dry flow), with the balance being N₂; 20 vol % H₂O (based on wet flow).

oxides and magnesium oxides start to make a greater contribution to H₂S removal.

Besides hydrogen and H₂S, carbon dioxide (CO₂) is usually present in the gases obtained from the auto-thermal reforming of hydrocarbons. Figure 9 shows the effect of CO₂ concentration in the feed gas mixture on the H₂S capture capacity of ZnO. The dynamic capacity gradually decreases from 0.239 g S/100 g ZnO to 0.213 g S/100 g ZnO as the CO₂ concentration increases in the range of 0–12 vol % (see Figure 9, Table 4). The observed trend is in agreement with that from the results of Sasaoka.¹³

From a qualitative evaluation based on the data obtained in this work, the negative effect of CO₂ is smaller than that of H₂O. The negative effect of water is easier to understand, because it is a product of the reaction between H₂S and ZnO. Although CO₂ is neither a reactant nor a product in the reaction between ZnO and H₂S, CO₂ showed an inhibiting effect on H₂S capture by ZnO in the presence of H₂O. This may be attributed to competitive adsorption between H₂S and CO₂ in the presence of steam. The aforementioned results indicate that the increase of water concentration and the increase of CO₂ concentration in the feed gas lead to lower capacities of ZnO for H₂S capture.

Table 5. Physical Properties of Fresh and Used Engelhard ZnO Absorbent and Sulfur Distribution along the Bed after 177 h of Operation at 300 °C, SV = 2660 h⁻¹, 8 ppmv H₂S, 34.4% H₂, and 20% H₂O, with the Balance Being N₂

sample ^a	pore volume (mL/g)	surface area (m ² /g)	porosity (%)	peak pore radius (Å)	sulfur content (wt %)
fresh	0.2839	53.13	49.37	60	0
1st part of the bed	0.2678	47.69	49.17	80	0.87
2nd part of the bed	0.3010	54.78	57.25	90	0.08
3rd part of the bed	0.2664	39.16	49.81	90	0.06
4th part of the bed	0.2984	64.62	65.31	90	0.03

^a The "1st part of the bed" is the region where the gas mixture enters the absorbent bed.

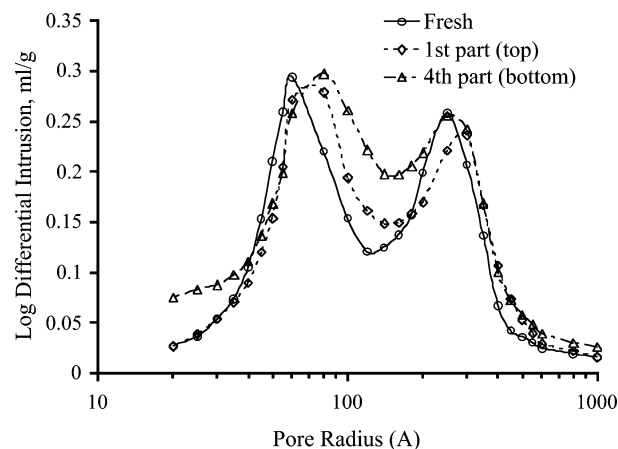


Figure 10. Pore-size distribution of ZnO-based extrudates from Engelhard: (○) fresh sample and after H₂S breakthrough ((◇) 1st part of the bed and (△) 4th part of the bed). Test conditions for H₂S removal: 300 °C; 2660 h⁻¹; 8 ppmv H₂S and 34.4% H₂, with the balance being N₂.

During the reaction between ZnO and H₂S, S ions substitute for O atoms in the lattice of ZnO, causing expansion of the absorbent, because the ionic radii of the O²⁻ and S²⁻ anions are 1.40 and 1.84 Å, respectively. The grains of ZnO in the absorbent becomes bigger after reaction with H₂S, which may cause the reduction of pore volume. However, the dynamic capacity of the absorbent was so low in the case of the 3-mm extrudates (0.417 g S/100 g ZnO; see Table 2) that no significant difference in pore volume has been observed using mercury porosimetry (see Table 5, Figure 10). The front part of the bed, which contains the highest concentration of sulfur (0.87 wt %), had a slightly smaller pore volume than the "fresh" absorbent but exhibited a shift in the bimodal pore-size distribution toward larger peak pore radii, when compared to the front part (top) of the bed. The pore volume and pore-size distribution of used absorbent particles from the other parts of the bed did not change significantly. The other parts of the absorbent beds had very low sulfur contents (0.08–0.03 wt %). Thus, after the feed gas flows through the first part of the bed, the H₂S concentration will decrease, and this leads to a lower H₂S concentration gradient which could lead to a lower degree of ZnO utilization. These results also suggest that only a small portion (layers of molecules) of the absorbent near the surface of the ZnO crystal particles are involved in the chemical reaction that is limited by gas diffusion into the solid particles.

Conclusions

This experimental study on H₂S capture from steam-containing gas mixtures, using ZnO-based absorbents, has led to the following conclusions:

(1) For the first time, the performance of ZnO-based absorbents has been comparatively studied at low H₂S concentrations (1–8 ppmv range), high space velocity (2660–8775 h⁻¹), and low-temperature range (300–400 °C) in the presence of steam (13–20 vol % H₂O).

(2) Differences in formulation and preparation techniques can have great impacts on the ZnO-based absorbent, in regard to H₂S uptake.

(3) The preparation technique that uses pretreatment in ammonium carbonate can lead to ZnO with superior morphology and higher surface area; an absorbent material that is based on such ZnO can effectively capture H₂S from reformat and provide an extremely low H₂S outlet concentration (<20 ppbv). Such ZnO-based absorbent material can be used as a polishing bed in fuel cell processors where high-purity hydrogen is required.

(4) A decrease in the feed-gas temperature increases the sulfur-capturing capacity of the ZnO sample significantly. The absorbent should preferably be operated at relatively low temperatures to achieve best performance.

(5) An increase in steam (H₂O) concentration decreases the H₂S capture and can cause the release of previously captured H₂S, because of a shift in the equilibrium of the reaction $\text{ZnO(s)} + \text{H}_2\text{S(g)} \leftrightarrow \text{ZnS(s)} + \text{H}_2\text{O(g)}$ toward ZnO and H₂S.

(6) A greater sulfur-capturing capacity of ZnO was observed at greater inlet H₂S concentrations and lesser space velocities.

(7) An increase in carbon dioxide (CO₂) concentration in the steam-containing gas mixture in the range of 4–12 vol % decreases the sulfur-capturing capacity of ZnO.

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