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H_2S removal with ZnO during fuel processing for PEM fuel cell applications

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Abstract

The efficacy of using ZnO as an absorber for the removal of H_2S from small fuel processor steam reformate streams was examined. At temperatures below 300 °C, H_2S can in principle be reduced to below 100 ppbv, required for safe operation of PEM fuel cells. The ZnO adsorbent performed predictably based on ZnO-H_2S-ZnS-H_2O equilibria with steam, hydrogen, and CO_2 in the feed. However, addition of CO even at levels as low as 1 vol% drastically lowered the sulfur removal capability of the ZnO. This is consistent with the formation of COS by the reaction $H_2S + CO = H_2 + COS$. ZnO is not an efficient absorber for COS. Indirect evidence is also provided for the formation of COS via the reaction $CO_2 + H_2S = COS + H_2O$, which can occur in special cases when CO_2 is present but neither H_2O nor CO is present in the feed. The potential for COS formation compromises the ability of ZnO to deliver very low sulfur concentration reformate.

Keywords: Fuel processor; ZnO; H_2S; Absorbent; Reformate; COS

1. Introduction

On-board fuel processing of commercially available liquid hydrocarbon fuels is being investigated as a means to supply hydrogen for polymer electrolyte membrane (PEM) fuel cell-based auxiliary power units [1]. If sulfur is not removed from these fuels prior to processing, the catalysts in the fuel processor as well as the fuel cell itself are susceptible to poisoning. The amount of sulfur that can be tolerated in any of the steps (reforming, water gas shift, selective CO oxidation) depends on the catalyst, conditions, and even mode of operation (e.g., partial oxidation versus steam reforming). Among these, the low temperature water gas shift catalyst has the lowest tolerance toward sulfur and will in some sense act as a guard bed for the downstream processes. For PEM application, the sulfur level in the hydrogen-rich fuel needs to be less than 100 ppb [2]. Although ultra-low sulfur fuels may be employed for these systems after 2006, the sulfur levels in these fuels (~30 ppmw of sulfur in gasoline and ~15 ppmw sulfur in diesel) are still too high. In this work, we have measured the performance of a commercial H_2S absorbent, ZnO, as a desulfurizer for this system. Although ZnO has been well-studied with hydrodesulfurized feedstocks [3–5], the performance of ZnO in removing sulfur from steam reformate in small on-board units at high space velocities does not appear to have been studied in detail.

If a single ZnO bed is to be employed for H_2S removal, it most likely will need to be located upstream of the low temperature water gas shift catalyst and operated at or below 300 °C, since the low temperature shift catalyst is extremely sensitive to sulfur concentration and strongly adsorbs H_2S. Our work has focused on determining the efficacy of lowering sulfur concentrations to 100 ppbv with ZnO over the temperature range 150–250 °C, in order to determine whether ZnO is kinetically capable of realizing H_2S concentrations significantly below 100 ppbv. For increased understanding of the role of the various feed components, we employed several gas compositions in addition to that anticipated to be processed by the low temperature water gas shift (LTWGS) catalyst.

2. Experimental

The test setup (Fig. 1) employed a small fixed bed reactor (quartz tube, 3.9 mm i.d.), which was heated by a small clam-shell furnace. The catalyst bed length to diameter ratio was five. Reactant gases (H_2, 50% CO in He, CO_2, 100 ppmv H_2S in He) were metered using mass flow controllers to achieve the desired

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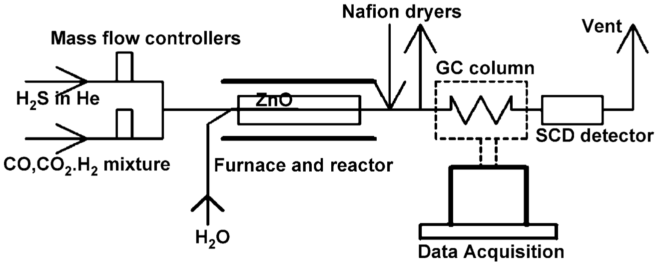

Fig. 1. Schematic of test setup.

reformate composition. Water was introduced using a HPLC pump, vaporized inside the furnace and mixed with the heated gas feed upstream of the ZnO absorbent bed. Water vapor was subsequently removed using two Nafion dryers (Perma Pure LLC) after the ZnO bed to facilitate chromatographic measurement. The analytical system comprised a HP6890 gas chromatograph equipped with a sulfur chemiluminescent detector (SCD). A 7-m, 320-μm i.d., uncoated silica capillary column was mounted inside the GC oven. This provided for very rapid chromatographic analysis to enable frequent sampling and more accurate determination of H_2S breakthrough capacity. However, it did not allow for sulfur speciation (e.g., separation of H_2S from COS). A six-port sampling valve equipped with an air actuator was used to make automatic injections into the GC. The sample loop volume was 1 ml. The injector, GC column, and valve box were all held at 30 °C. During the experimental run the analytical system operated continuously, sampling the effluent every 3 min. The detection limit of the system to total sulfur was approximately 50 ppb.

ZnO (Süd-Chemie; G-72E) was used in this work. Typical measurements employed a 0.2 g ZnO sample, sieved to 60–80 mesh. Experiments were carried out in the relatively low temperature range 150–250 °C, consistent with the desire to obtain equilibrium H_2S below 100 ppbv. Two sulfur breakthrough capacities were measured, one at 100 ppb in the effluent and the other at 1 ppm in the effluent. Four different dry gas mixtures plus steam were used to simulate feed compositions similar to what would be seen by the high temperature water gas shift (HTWGS) catalyst, the LTWGS catalyst, the preferential oxidation (PROX) catalyst, and the PEM fuel cell. A feed gas without either CO or CO_2 was also used to provide a performance comparison. Table 1 gives the composition of the dry gas mixtures, to which steam was added.

Table 1
Gas volume composition of feeds employed, dry basis

Feed	H_2S[a] (ppm)	CO[b] (%)	CO_2[c] (%)	H_2[d] (%)	Balance
1	25	0	0	75	He
2	25	0	21	54	He
3	25	1	20	53	He
4	25	4	17	50	He
5	25	12	9	42	He

[a] H_2S source: 100 ppmv H_2S in He.
[b] CO source: 50% CO in He.
[c] CO_2 source: 100% CO_2.
[d] H_2 source: 100% H_2.

3. Results and discussion

H_2S absorption by ZnO is considered to be controlled by the following reaction [3]:

$$ZnO + H_2S \leftrightarrow ZnS + H_2O \qquad (1)$$

This is an exothermic reaction, and the equilibrium H_2S concentration is determined by the temperature, the H_2O partial pressure, and to a lesser extent the phase of the zinc oxide. Equilibrium H_2S concentration for sphalerite ZnO is shown in Fig. 2. When there is 30% H_2O in the feed, as is the case with the steam reformate, thermodynamically it is impossible to reduce the sulfur level to less than 100 ppb at temperatures above 315 °C.

At lower temperatures (<250 °C), absorption kinetics are slower but ZnS equilibrium is more favorable. If the kinetics of H_2S absorption are sufficiently rapid, concentrations well below 100 ppb, with reasonable H_2S capacity, should in principle be achievable.

Table 2 summarizes the sulfur absorption performance of the ZnO sample under varying temperature and feed compositions. Experiment 1 shows that the H_2S adsorption capacity at 200 °C is substantial when only H_2 and H_2O are present, and experiment 2 shows that the presence of CO_2 under these conditions has no effect of H_2S uptake. On the other hand, experiments 3–5 show that the presence of CO in the feed drastically decreases the apparent H_2S breakthrough capacity of ZnO, and this capacity progressively decreases with increasing CO content. Experiments 6–8 show the same effect at 150 °C. Experiment 9 shows that there is no benefit of higher operating temperature (250 °C) on ZnO performance when 4% CO is present in the feed, indicating that the limitations to H_2S adsorption are not based on slow kinetics at these lower temperatures. For the feed with 4% CO, no matter which test parameters (temperature, space velocity, H_2O concentration) are varied, it seems impossible to achieve 100 ppb H_2S in the exit gas. It is interesting to note, in comparing the results of experiments 2 and 3, that ZnO is not active toward the water gas shift reaction. Otherwise, if the reverse shift occurred with feed 2, generating CO, this should result in a decrease in capacity compared with experiment 1.

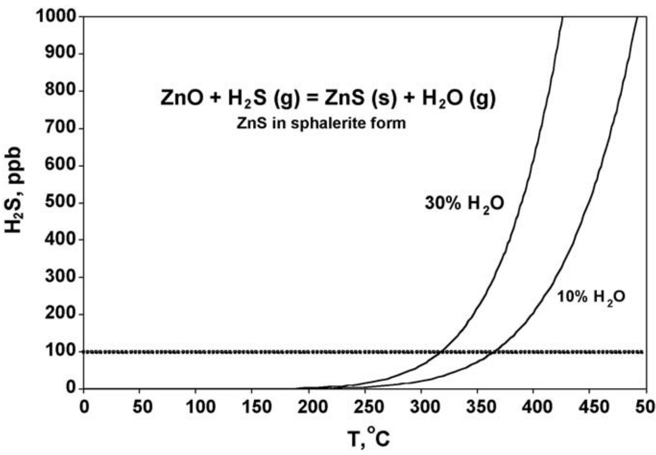

Fig. 2. Calculated thermodynamics of H_2S absorption by ZnO (sphalerite).

Table 2
Sulfur absorption performance on ZnO

Experimental parameter	Temperature (°C)	Experiment no.	Feed	CO, dry basis (%)	CO_2, dry basis (%)	H_2O, in total feed (%)	GHSV (h^{-1} × 1000)	S uptake, (wt.% at 100 ppb)[a]	S (uptake, wt.% at 1 ppm)[a]
CO-CO_2 concentration effect at 200 °C	200	1	1	0	0	30	75	10.5	19.0
	200	2	2	0	21	30	75	11.0	21.1
	200	3	3	1	20	30	75	4.0	6.8
	200	4	4	4	17	30	75	1.1	2.2
	200	5	5	12	9	30	75	0.2	0.7
CO-CO_2 concentration effect at 150 °C	150	6	2	0	21	30	75	13.1	16.5
	150	7	3	1	20	30	75	2.7	6.3
	150	8	4	4	17	30	75	0.2	1.5
T effect for 4% CO feed	150	8	4	4	17	30	75	0.2	1.5
	200	4	4	4	17	30	75	1.1	2.2
	250	9	4	4	17	30	75	0.1	0.3
H_2O effect for 4% CO feed	200	10	4	4	17	0	75	0.1	0.6
	200	11	4	4	17	10	75	0.6	6.3
	200	4	4	4	17	30	75	1.1	2.2
GHSV effect for 4% CO feed	200	12	4	4	17	30	15	1.0	1.6
	200	4	4	4	17	30	75	1.1	2.2
	200	13	4	4	17	30	200	0.2	0.6

[a] S capacity is defined as (g S absorbed/g ZnO) × 100 at sulfur concentration breakthrough points.

Although Table 2 shows a predominant negative effect of CO, it appears that the H_2O concentration has an effect as well on ZnO performance when carbon oxides are present. Comparing experiments 10, 11, and 4, most notably at the 100 ppb breakthrough point, there is a surprising apparent increase in H_2S capacity with an increase in H_2O in the feed, counter to the arguments expressed earlier with respect to reaction (1). Notably, the water-free case (experiment 10) shows very poor performance. Experiment 2 was then repeated (21% CO_2 and 30% H_2O), but at 150 °C rather than 200 °C. When H_2O flow was temporarily stopped during the run, the sulfur concentration increased immediately, as shown in Fig. 3. Resumption of feed water resulted in measured sulfur concentration returning to initial levels. This result also appears inconsistent with reaction (1).

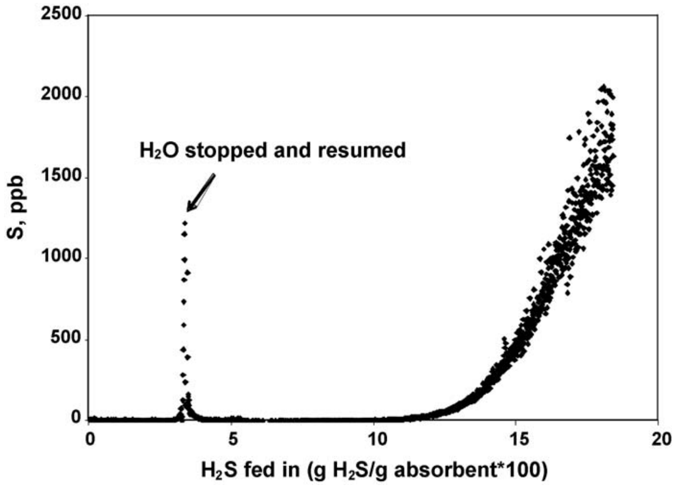

Fig. 3. Sulfur absorption on ZnO at 150 °C, 75 K h^{-1} GHSV, 30% H_2O, 70% dry feed composition 2, showing effect of water on measured sulfur in effluent.

Finally, experiments 12, 4 and 13 show that there is no increase in apparent H_2S capacity at low space velocities, but at the high space velocity of 200 K h^{-1}, capacity does show a decrease.

It is known that H_2S can react with CO or CO_2 to form COS through the following two reactions [6–8]:

$$H_2S + CO \leftrightarrow COS + H_2 \tag{2}$$

$$H_2S + CO_2 \leftrightarrow COS + H_2O \tag{3}$$

The equilibrium COS concentrations under the tested conditions can be calculated for both reactions and the results are summarized in Table 3. HSC Chemistry 5.11 (Outokumpu Research Oy, Pori, Finland) software was used for these calculations. The concentrations of CO, CO_2, and H_2O in the feed gas were used as equilibrium concentrations, since CO-CO_2 equilibration would not be expected in the absence of the water gas shift reaction over ZnO. The sulfur breakthrough capacities appear to be strongly correlated with the calculated COS concentrations, as described by reaction (2). We believe that the apparent low H_2S capacities are actually the result of COS in the product, since ZnO cannot remove COS efficiently [8], and our analytical system was not set up to distinguish between H_2S and COS (it proved difficult to obtain a COS

Table 3
COS equilibrium concentrations as predicted from reactions (2) and (3) (see text)

Temp, (°C)	Expt no.	Feed	CO, dry basis (%)	CO_2, dry basis (%)	H_2O, in total feed (%)	COS, at equilibrium (ppb)[a]	COS, at equilibrium (ppb)[b]
200	1	1	0	0	30	0	0
200	2	2	0	21	30	0	9
200	3	3	1	20	30	56	8
200	4	4	4	17	30	234	7
200	5	5	12	9	30	815	4
150	6	2	0	21	30	0	3
150	7	3	1	20	30	73	3
150	8	4	4	17	30	308	3
250	9	4	4	17	30	189	15
200	10	4	4	17	0	234	~25000[c]
200	11	4	4	17	10	234	21
200	12	4	4	17	30	234	7
200	13	4	4	17	30	234	7

[a] Based on reaction (2).

[b] Based on reaction (3).

[c] All H_2S in feed is converted to COS.

standard). Fig. 4 shows the relationship between the measured 100 ppb breakthrough sulfur capacity and equilibrium COS concentration calculated from reaction (2).

On the other hand, reaction (3) can explain the very low sulfur breakthrough capacities with ZnO using a feed containing 4% CO, 17%CO_2, and 0% H_2O (experiment 10). Reaction (3) can also help explain the phenomena shown in Fig. 3, wherein sulfur in effluent increases rapidly as a result of turning off the water to the system. When the H_2O partial pressure is low, reaction (3) shifts to the right hand side, and more COS forms. It should be noted that the calculation is based on no sulfur absorption on the ZnO bed. Due to H_2S absorption on ZnO, reactions (2) and (3) equilibria should shift to the left, which will decrease the COS concentration in the system. It needs to be stressed that thermodynamics should only be used as a guide, as the total sulfur breakthrough capacities are determined by both the thermodynamics and kinetics of reactions (1–3).

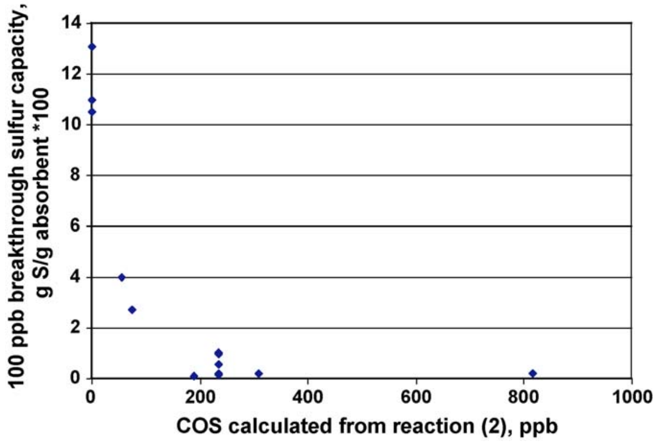

Fig. 4. Relationship between 100 ppb breakthrough sulfur capacity and equilibrium COS concentration calculated from reaction (2): $CO + H_2S = COS + H_2$.

4. Summary

We have carried out experiments to determine the feasibility of using ZnO as an absorbent to remove H_2S from steam reformate streams. In the absence of CO, our ZnO sample was able to remove H_2S with high capacity at 200 °C via the reaction $ZnO + H_2S = ZnS + H_2O$. With CO present in the feed, however, the sulfur absorption capacity of ZnO was significantly lowered, with higher CO levels correlating with decreasing breakthrough sulfur capacity. These results are consistent with the reaction of CO with H_2S to produce COS and H_2. It is known that ZnO is not effective in removing COS. We also observed indirect evidence for the production of COS from the reaction $CO_2 + H_2S = COS + H_2O$: feeds containing only CO_2 and water showed an immediate loss of ZnO sulfur capacity when water feed was removed, but the sulfur removal capacity was restored when water feed was resumed. It appears that the ability of ZnO to function as an effective sulfur adsorbent with H_2S-containing syngas feeds is compromised by the formation of COS, which is catalyzed by ZnO.

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