H_2S removal with ZnO during fuel processing for PEMFC applications

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Introduction

On-board fuel processing of liquid hydrocarbon fuels is being investigated to supply hydrogen for PEM fuel cell-based auxiliary power units [1]. For such a system, if sulfur is not removed from the liquid phase, removal of sulfur as H_2S from the reformate is a key step since downstream catalysts and the fuel cell itself can be poisoned by a small amount of H_2S in the feed. For PEM application, the sulfur level in the hydrogen fuel needs to be less than 100 ppb [2]. Although ultra-low sulfur fuels may be employed for these systems, 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 measured the performance of commercial H_2S absorbent, ZnO, as a desulfurizer for this system. Although ZnO has been well-studied with hydrodesulfurized feedstocks, the performance of ZnO in removing H_2S from reformate in small onboard units and with high space velocities does not appear to have been thoroughly studied.

Materials and Methods

The test setup employed a small fixed bed reactor (quartz tube, 3.9 mm i.d.), which was heated by a small clam-shell furnace. Reactant gases (H_2, 50%CO in N_2, CO_2, 100 ppm H_2S in He) were metered using mass flow controllers. Water was introduced using a HPLC pump and was vaporized inside the furnace before the ZnO absorbent bed, and was removed using two Nafion dryers (from 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). The detection limit of the system to H_2S is approximately 50 ppb. Süd-Chemie ZnO (G-72E) was used in this work. Typical measurements employed a 0.2 g ZnO sample, sieved to 60-80 mesh. Four dry gas mixtures were used to simulate feeds to the high temperature water gas shift (WGS) reactor, to the low temperature WGS reactor, to the PROX reactor, and to the fuel cell respectively; each feed was spiked with 25 ppm H_2S. Two H_2S breakthrough capacities were measured, one at 100 ppb in the effluent and the other at 1 ppm in the effluent.

Results and Discussion

Table 1 gives the H_2S absorption performance of the ZnO sample in feeds with different CO-CO_2 concentrations. Normally H_2S absorption by ZnO is controlled by the following reaction:

$$ZnO + H_2S \leftrightarrow ZnS + H_2O$$

This is an exothermic reaction, and the equilibrium H_2S concentration is determined by the structure of the ZnS product, the temperature, and the H_2O partial pressure. However, the results given in Table 1 clearly indicate that the presence of CO greatly decreases the H_2S breakthrough capacity of ZnO. After the H_2S absorption tests where CO was present in the feed, the ZnO changed to a grey color, indicating carbon formation occurred on the ZnO surface, presumably via the Boudouard reaction:

$$2CO\ (g) \leftrightarrow CO_2\ (g) + C\ (s)$$

Not only does the presence of CO affect the breakthrough capacity, but CO_2 as well. Figure 1 shows that with significant levels of CO_2, the presence of water is critical to maintaining low H_2S levels. When H_2O was removed, the H_2S level increased. This appears to be a reversible effect since re-adding steam to the feed again reduced H_2S to low levels.

Table 1. H_2S absorption performance on ZnO in feeds with different CO-CO_2 concentrations (200°C, 75K hr^{-1} GHSV, 30% H_2O in total feed)

CO% in Dry Feed Gas	CO_2 % in Dry Feed	H_2S % BT capacity at 100 ppb	H_2S % BT capacity at 1 ppm
0	0	10.5	19.0
0	21	11	21.1
1	20	4.0	6.8@700ppb
4	17	1.05	2.16
12	9	0.21	0.71

* H_2S capacity is defined as g.H_2S absorbed/g. ZnO *100 at H_2S breakthrough points.

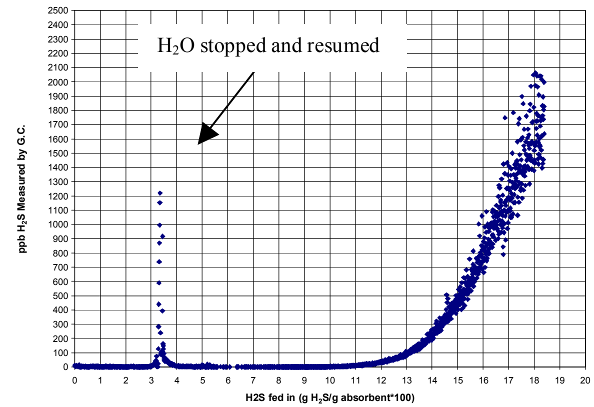

Figure 1. H_2S absorption on ZnO at 150°C, 75K hr^{-1} GHSV, 30% H_2O, and in 25 ppm H_2S, 21%CO_2, 53% H_2, 26% He dry gas feed

Significance

These results show that although ZnO is generally considered to be an effective absorbent for H_2S removal, it is not capable to provide less than 100ppb in the effluent from a steam reformate stream, as CO and CO_2 adversely affect breakthrough capacity.

References

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2. Song, C.S. *Catalysis Today* 77, 17 (2002).