

ACTIVE CARBONS AS CATALYSTS FOR THE OXIDATION OF HYDROGEN SULPHIDE

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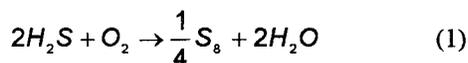
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Introduction

The potential of activated carbons for the removal of hydrogen sulphide has been demonstrated in the literature [1-6]. It was found that the removal of hydrogen sulphide is achieved by adsorption and oxidation processes [5]. However, the removal mechanisms are still ambiguous.

At low temperatures the reaction mechanism was proposed as [4]:



The oxidation of hydrogen sulphide was found to be dependent on the concentration of hydrogen sulphide, oxygen, and water, and on the temperature. While the effect of hydrogen sulphide, oxygen and temperature is quite straight forward, the effect of water on the catalytic oxidation of hydrogen sulphide is still uncertain. The argument on the effect of water arises from the mechanisms involved. Water was found to have an adverse effect by blocking the active sites [2]. Nevertheless, based on a liquid film model [3], water was found to enhance the reaction by dissolving hydrogen sulphide in water absorbed on the surface of carbon [6].

Even though the formal kinetics of the reaction has been studied by many research groups [2,6], the influence of the H₂S, O₂ and H₂O partial pressure on the reaction rate on carbon is not yet fully understood. The reaction mechanism might be simply explained by an oxidation-reduction mechanism [6]. A similar mechanism based on the reaction between adsorbed hydrogen sulphide and adsorbed oxygen has been proposed elsewhere [2]. The reaction order of hydrogen sulphide and oxygen was found to vary between zero and one. A Langmuir-Hinshelwood model, in which a surface-reaction was a rate determining step was found to agree well with the data obtained by Ghosh and

Tollefson [2]. However, these mechanisms fail to explain the effect of water on the oxidation rate of hydrogen sulphide.

Thus, it seems that there is a lack of understanding in the mechanism of hydrogen sulphide oxidation on carbon in the presence of water. This has led to the present investigation of this particular reaction.

Experimental

The reduction-oxidation of hydrogen sulphide has been carried out in a differential packed bed reactor. Mixtures of hydrogen sulphide, oxygen and helium were prepared with the aid of mass flow controllers: where necessary the gases could be humidified by passage through bubblers containing water maintained at constant temperatures. The gas mixture then passed through a reactor (0.6 id). Exit gases were separated using a GS Q capillary column and analysed using a flame photometric detector. This allowed the determination of hydrogen sulphide and sulphur dioxide. Adsorption/back titration showed that there were no significant amounts of sulphur trioxide in the reactor exit gas.

Operating conditions covered the following ranges: H₂S concentration 5-35 ppm, O₂ concentration 0-21%, H₂O concentration 0-2.2% at 1 atm and 298 K.

Results and Discussion

It was found that the rate of hydrogen sulphide oxidation increased with increasing hydrogen sulphide and oxygen partial pressure (figure 1). It was noticed that, even when the oxidation of hydrogen sulphide was carried out in excess of oxygen, the oxidation rate was still dependent on oxygen partial pressure.

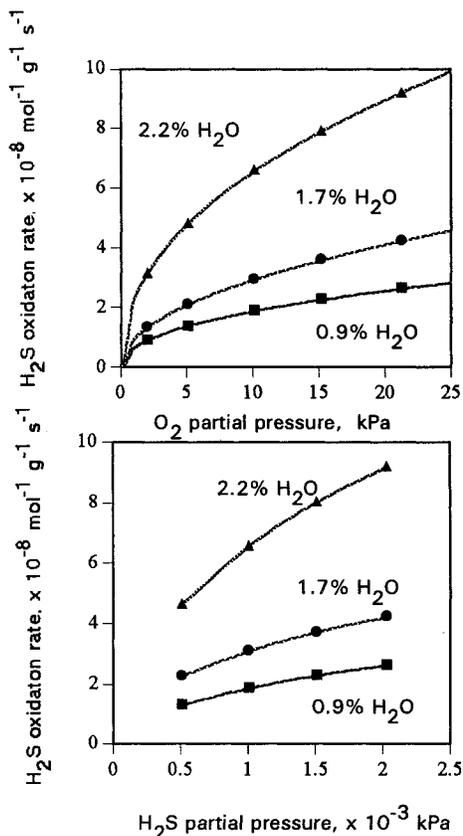


Figure 1. The effect of H_2S and O_2 partial pressure on the oxidation rate.

Water in the carbon was found to have a positive effect on the oxidation rate. The rate of hydrogen sulphide oxidation increased with increasing water partial pressure. By using a power law model, the results showed that the order of reaction with respect to water was found to be 1.28, while the orders with respect to hydrogen sulphide and oxygen were 0.48 and 0.47 respectively. It is apparent that the rate of hydrogen sulphide oxidation is strongly affected by the water partial pressure.

Surface-reaction kinetic models were investigated. The results showed that the predictions of a Langmuir-Hinshelwood model, in which a surface-reaction was a rate determining step, agreed well with the data obtained in the absence of water. However, the proposed kinetic models failed to explain the effect of water.

It was found that the reaction rate increased linearly with increasing amounts of water condensed in the micropores of carbon. Thus it is suggested that the most plausible mechanism for the oxidation of hydrogen sulphide involves reaction in a water film. It is proposed that the oxidation of hydrogen sulphide occurs via the reaction between HS^- , either adsorbed or present in the

water film, with sorbed O_2 to yield water and solid sulphur. Carbon is important in providing a pore matrix for condensation of water.

Pseudo surface kinetic models were then proposed. The results showed that pseudo Rideal-Eley Models, in which the reaction between adsorbed oxygen and HS^- dissolved in water is the rate-determining step, predicts a rate of hydrogen sulphide oxidation of the form:

$$-r_{H,S} = \frac{k_1 P_{O_2}^{1/2} P_{H,S}^{1/2}}{(1 + k_2 P_{O_2}^{1/2})} \quad (2)$$

Experimental results agreed with this prediction. Thus, it is the pores in the carbon that are primarily responsible for the catalytic activity.

Conclusions

Activated carbons were found to be active for the abatement of hydrogen sulphide via adsorption and oxidation processes. The oxidation of hydrogen sulphide was found to occur in a water film. The reaction mechanism could be expressed by pseudo surface-reaction models. The reaction between adsorbed oxygen and HS^- was assumed to be the rate-determining step and this gave predictions that agreed with experimental observations.

Acknowledgments

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