

## Effect of Sulfur on Precious Metal Steam Reforming Catalysts.

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### Introduction

Sulfur is known to poison catalysts for many reactions, in particular steam reforming. Even when present in the hydrocarbon feedstock in small quantities, ppb levels, sulfur can have detrimental effects with increasing time on stream. Currently, most of the work regarding sulfur poisoning has been carried out on nickel catalysts; however advances in steam reforming could mean that precious metal catalysts are an attractive option for the future. This study looks at sulfur poisoning of precious metal catalysts, namely Pt/Al<sub>2</sub>O<sub>3</sub>. To determine how the identity of the sulfur species affected the catalyst two different poisons were chosen, hydrogen sulfide and methanethiol. Steam reforming of ethane has been studied to determine how the sulfur molecules affect activity and selectivity.

### Materials and Methods

The catalyst was prepared by impregnating the pre-dried support (alumina heated to 1173 K for 2h, S.A. 104 m<sup>2</sup>g<sup>-1</sup>) to incipient wetness with an aqueous solution containing the precursor salt (H<sub>2</sub>PtCl<sub>6</sub>) to give a weight loading of 0.2 %. The catalyst had a BET area of 107 m<sup>2</sup>g<sup>-1</sup> and a Pt dispersion of 18 %. Steam reforming experiments were carried out using a fixed bed micro reactor. Ethane and steam were fed into the reactor at a ratio of 1:2.5 to limit carbon laydown. The reaction pressure was 20bar and temperature 600°C. On-line G.C. was used to analyse the products. The sulphur species was introduced into the system by dissolving the relevant gas into the feed water. The concentrations of sulphur in water were 11.2ppm and 5.6ppm.

### Results and Discussion

When methanethiol is introduced into the system (between dotted lines in Fig.1) the catalyst deactivates rapidly. However once the poison is removed from the feed, the activity recovers to the expected level (Fig.1).

When hydrogen sulfide is introduced deactivation of the catalyst is apparent, but to a lesser extent than methanethiol. This is evident with all the products (table 1).

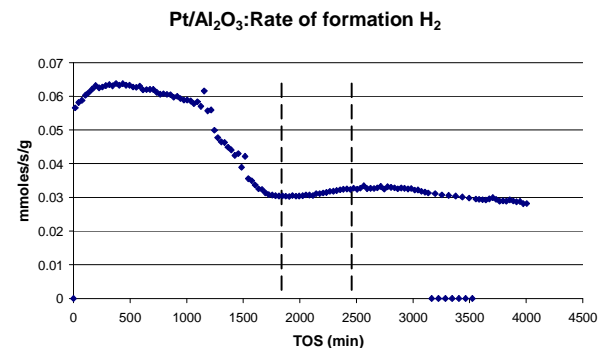


Figure 1. Effect of 11.2ppm methanethiol on the rate of H<sub>2</sub> formation.

Product	H <sub>2</sub> S	CH <sub>3</sub> SH
H <sub>2</sub>	8	11
CO	2	9
CO <sub>2</sub>	9	14
CH <sub>4</sub>	16	24

Table 1. Comparison of deactivation rate constants ( $\times 10^{-4}$ ) for each product

From analysis of the deactivation of each product it is clear that methane formation is most affected, followed by hydrogen and carbon dioxide, which deactivate at the same rate, whilst, carbon monoxide formation showed very little deactivation. This suggests that some reactions are being poisoned more readily than others, leading to the proposal of the following deactivation order:

Hydrogenolysis/methanation > Water-gas shift > Steam reforming

### Significance

The study shows that the rate of Pt/Al<sub>2</sub>O<sub>3</sub> deactivation is dependent on the identity of the poison, with methanethiol being more deleterious than hydrogen sulphide probably due to sulphur and carbon laydown. The overall deactivation process is complex because of the different reactions that are occurring and their different susceptibility to poisoning.