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# Ethane Steam Reforming over a Platinum/Alumina Catalyst: Effect of Sulfur Poisoning

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**ABSTRACT:** In this study we have examined the adsorption of hydrogen sulfide and methanethiol over platinum catalysts and examined the effect of these poisons on the steam reforming of ethane. Adsorption of hydrogen sulfide was measured at 293 and 873 K. At 873 K the adsorbed state of hydrogen sulfide in the presence of hydrogen was SH rather than S, even though the Pt:S ratio was unity. The effect of 11.2 ppm hydrogen sulfide or methanethiol on the steam reforming of ethane was studied at 873 K and 20 barg. Both poisons deactivated the catalyst over a number of hours, but methanethiol was found to be more deleterious, reducing the conversion by almost an order of magnitude, possibly due to the co-deposition of sulfur and carbon. Changes in the selectivity revealed that the effect of sulfur was not uniform on the reactions occurring, with the production of methane reduced proportionally more than the other products, due to the surface sensitivity of the hydrogenolysis and methanation reactions. The water-gas shift reaction was affected to a lesser extent. No regeneration was observed when hydrogen sulfide was removed from the feedstream in agreement with adsorption studies. A slight regeneration was observed when methanethiol was removed from the feed, but this was believed to be due to the removal of carbon rather than sulfur. The overall effect of sulfur poisoning was to reduce activity and enhance hydrogen selectivity.

## 1. INTRODUCTION

Steam reforming is the most widely practiced process for the production of hydrogen, accounting for the production of 96% of on-purpose hydrogen. It is a highly endothermic reaction and is favored at high temperatures and low pressure. The nickel catalysts used are robust but are sensitive to poisons such as sulfur, and it is usual for there to be a sulfur removal process upstream of the reformer.

Sulfur is defined as a nonspecific catalyst poison that can dramatically reduce catalytic activity (for general reviews, see refs 1 and 2). At low concentrations, however, it has been used to modify catalytic properties. These effects are explained by making use of both electronic and geometric aspects of catalytic reactions on surfaces. For example, adsorbed sulfur will poison the site on which it is adsorbed, and it may also poison a larger number of sites by removing a geometrical degree of freedom from the surface.<sup>1,2</sup> In addition the formation of a bond between a metal atom in an array and a sulfur atom may affect the ability of neighboring metal atoms to form bonds of the correct strength to allow a catalytic reaction to occur. This type of behavior has been well-understood for many years, at least empirically, and has been used to good effect in the reforming industry.<sup>3</sup>

Sulfur poisoning studies regarding steam reforming have mostly been conducted using nickel catalysts; indeed, we could find very few examples of studies of the effect of sulfur on steam reforming over precious metals. Rostrup-Nielsen showed the effect of sulfur poisoning on the specific activity of 25 wt % Ni/MgOAl<sub>2</sub>O<sub>3</sub> during steam reforming of ethane at 775 K.<sup>4</sup> The specific activities based on the remaining Ni surface area are reasonably constant over a wide range of sulfur coverage, providing evidence that chemisorbed sulfur poisons by blocking the metal surface for adsorption of reactants. In a later

publication Rostrup-Nielsen reviewed the effect of sulfur on nickel catalysts.<sup>5</sup>

The effect of altering the conditions of steam reforming on the sulfur tolerance of a Rh/La–Al<sub>2</sub>O<sub>3</sub> catalyst was recently studied by Krause et al.<sup>6</sup> The effect of temperature and the steam-to-carbon ratio were examined, and a significant improvement in the sulfur tolerance of the catalyst was observed when the reaction temperature was increased from 973 to 1073 K. It was expected that the decrease in sulfur coverage with increasing reaction temperature would help improve the sulfur tolerance of the catalyst; however, the authors attributed most of the improvement to the ability of the catalyst to gasify carbon as the amount carbon decreased from 44.6 to 4.4 wt % on going from 973 to 1073 K.

Recent studies have indicated that the activity of platinum in steam reforming is similar to that of rhodium,<sup>7</sup> and both are well-known to be more active than nickel, although not yet commercially used. Nevertheless there has long been interest in using precious metals and platinum in particular as sulfur-tolerant steam reforming catalysts. In a patent from 1966,<sup>8</sup> low loaded platinum/alumina catalysts were shown to be active for steam reforming and with resistance to sulfur poisoning. A more recent patent in 2005 also reveals the use of platinum and other precious metals as improved steam reforming catalysts especially for heavier feedstreams.<sup>9</sup> In this study, which we believe to be the first to examine sulfur poisoning of steam reforming over a platinum catalyst, a low loading of platinum (0.2% (w/w)) was chosen as this was viewed as a more realistic

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loading for a commercial precious metal catalyst, while from the a wide range of possible sulfur containing species we chose the general motif of R-SH, looking initially at hydrogen sulfide (H-SH) and methanethiol (CH<sub>3</sub>-SH). The sulfur concentration was chosen at ~10 ppm as this value both was realistic and gave the opportunity to follow any deactivation over a sensible period of time.

## 2. EXPERIMENTAL SECTION

The catalyst used for steam reforming reactions was prepared by incipient wetness with an aqueous solution containing the precursor salt (H<sub>2</sub>PtCl<sub>6</sub>, Johnson Matthey). The alumina was prepared from Disperal boehmite (Sasol, S.A.; 180 m<sup>2</sup>g<sup>-1</sup>) by firing to 1173 K for 2 h followed by 1473 K for 5 h. The pore volume of the alumina, after firing, was 1 cm<sup>3</sup> g<sup>-1</sup>. Chloroplatinic acid was added to water, and a sufficient amount of solution added to the support to obtain a weight loading of 0.2% (w/w) Pt. The resulting catalyst was dried and calcined at 723 K for 4.5 h. The Brunauer-Emmett-Teller (BET) surface area of the catalyst was 107 m<sup>2</sup>g<sup>-1</sup>, and hydrogen chemisorption gave a Pt dispersion of 18%, which gives an average particle size of ~6 nm. X-ray diffraction (XRD) analysis of the reduced catalyst revealed no bands attributable to platinum.

Steam reforming reactions were carried out in a high-pressure microreactor. All tests followed the same initial procedure. The reactor was loaded with 0.5 g of catalyst and sealed and the system purged for an hour in a flow of 50 cm<sup>3</sup> min<sup>-1</sup> Ar. The system was then pressurized to 20 barg over a period of 2 h, during which the catalyst was heated to the reaction temperature of 873 K. Once at temperature and pressure, hydrogen was added to the gas stream until it matched the argon flow. The mixed stream of 50:50 H<sub>2</sub>:Ar was passed over the catalyst for 2 h to reduce the catalyst. After reduction, the Ar flow was switched off and steam (490 cm<sup>3</sup> min<sup>-1</sup>) was introduced, maintaining the H<sub>2</sub> flow to keep the gas mix reducing. This H<sub>2</sub>/H<sub>2</sub>O feed was maintained for 1 h to ensure the steam was well-established before introducing the hydrocarbon. Ethane was introduced over 15 min by gradually increasing the flow to 98 cm<sup>3</sup> min<sup>-1</sup>; the H<sub>2</sub> flow was then stopped. The steam to carbon ratio was 2.5:1. The first gas chromatograph (GC) analysis was taken 15 min after the full introduction of ethane, and thereafter analyses were taken every 30 min. The gases leaving the apparatus were monitored online and real-time via a Varian gas chromatograph, fitted with a CARBO XENTM 1010 PLOT column.

For introduction of poison to the catalysts, hydrogen sulfide and methanethiol were dissolved into distilled water, and the resultant solution was pumped into the system. Hence, once steady state was reached (normally after 17 h), the water being pumped into the system was changed for water with dissolved sulfur species. This water was pumped for 7 h before changing back to the normal distilled water. Two solutions were prepared; 11.2 ppm methanethiol and 11.2 ppm hydrogen sulfide.

Two further catalysts were prepared for adsorption studies, 1% (w/w) Pt/alumina and 1% Pt/silica. Both catalysts were prepared by incipient wetness of the two supports ( $\theta$ -alumina, surface area 101 m<sup>2</sup> g<sup>-1</sup>; silica, surface area 220 m<sup>2</sup> g<sup>-1</sup>) using Pt(NH<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub> as the precursor salt. The catalysts were dried and calcined at 773 K for 4 h.

Chemisorption studies were performed in a dynamic mode using a pulse-flow microreactor system in which the catalyst

sample was placed on a sintered glass disc in a vertical tube (8 mm i.d., down flow) inside a furnace. The reactant pulses were introduced into the gas stream immediately above the catalyst bed using a sample loop of identical dimensions to the reactor. Using this system the catalysts (typically 0.5 g) were reduced in situ in a flow of hydrogen (40 cm<sup>3</sup> min<sup>-1</sup>) by heating to 673 K at a rate of 10 K min<sup>-1</sup>. The catalyst was held at this temperature for 2 h. The catalyst was then purged with argon (30 cm<sup>3</sup> min<sup>-1</sup>) for 30 min and the catalyst cooled. The adsorbate gases were admitted by injecting pulses of known size (typically 24  $\mu$ mol) into the argon carrier-gas stream and hence onto the catalyst. In all cases the whole pulse was analyzed by online gas chromatograph-mass spectrometry (GC-MS). The amount of gas adsorbed, from any pulse, was determined from the difference between a calibration peak area and the peak area obtained following the injection of pulses of comparable size onto the catalyst. The detection limit for adsorption was 0.3  $\mu$ mol g<sup>-1</sup>. Adsorptions were followed using a gas chromatograph fitted with a thermal conductivity detector and molecular sieves 5A and Porapak Q columns.

Both the helium (BOC, 99.997%) and the 5% hydrogen in dinitrogen (BOC) were further purified by passing through a Chrompack gas-clean oxygen filter to remove any oxygen impurity, and a bed of Chrompack gas-clean moisture filter to remove any water impurity. Carbon monoxide (99.99% research grade), hydrogen sulfide (>99%), and methanethiol (>99%) were all used as received.

## 3. RESULTS

**3.1. Adsorption Studies.** The adsorption of carbon monoxide, hydrogen sulfide, and methanethiol was examined over the high weight-loading platinum catalysts. Multiple pulses of each gas were passed over the catalysts, as described in the Experimental Section, until no further adsorption was detected. Using this methodology the pressure of the pulse is always 1 bar and only strongly bound species are detected. In separate experiments no carbon monoxide adsorbed on the alumina or silica supports. The carbon monoxide adsorption gave metal dispersion figures of 96% for both Pt/alumina and Pt/silica assuming a Pt:CO ratio of 1:1. Hydrogen sulfide did not adsorb on the silica support but did adsorb on the alumina; hence, the adsorption data for the Pt/alumina catalyst had the support contribution subtracted from the total adsorption. The hydrogen sulfide adsorption data are reported in Table 1.

**Table 1. Hydrogen Sulfide Adsorption at 293 K**

catalyst	H <sub>2</sub> S adsorbed, $\mu$ mol g <sup>-1</sup>	H <sub>2</sub> :S(ads) <sup>a</sup>	dispersion, %
Pt/alumina	30.3	0.64	59
Pt/silica	44.6	0.69	87

<sup>a</sup>H<sub>2</sub> evolved during adsorption relative to H<sub>2</sub>S adsorbed

The adsorption of hydrogen sulfide was also studied at 873 K in the absence and presence of hydrogen. When the hydrogen sulfide was adsorbed in the presence of hydrogen, the ratio of the mix was 1:1. The results are shown in Tables 2 and 3. The amount of hydrogen sulfide adsorbed on the alumina at 873 K has been subtracted from the Pt/alumina adsorption in Tables 2 and 3. No adsorption took place on the silica.

Adsorption of methanethiol was attempted; however, direct analysis proved impossible due to interaction between the methanethiol and the GC. Nevertheless hydrogen was evolved when methanethiol was passed over the catalysts at 293 K.

**Table 2. Hydrogen Sulfide Adsorption at 873 K**

catalyst	H <sub>2</sub> S adsorbed, $\mu\text{mol}\cdot\text{g}^{-1}$	H <sub>2</sub> :S(ads) <sup>a</sup>	Pt:S(ads) <sup>b</sup>
Pt/alumina	68.1	1:0.81	1:1.3
Pt/silica	80.8	1:0.97	1:1.6

<sup>a</sup>Ratio of hydrogen evolved to sulfur adsorbed. <sup>b</sup>Ratio of Pt to sulfur adsorbed.

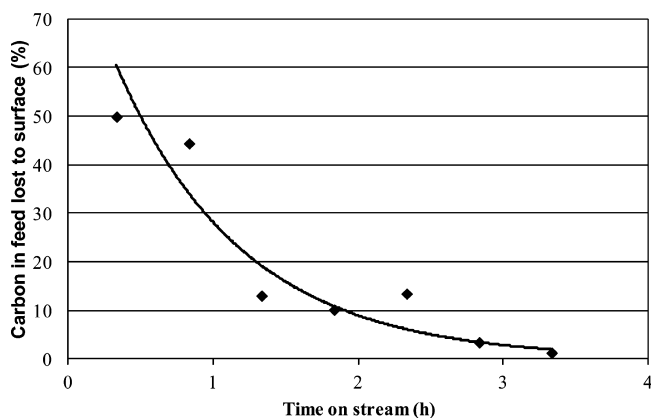
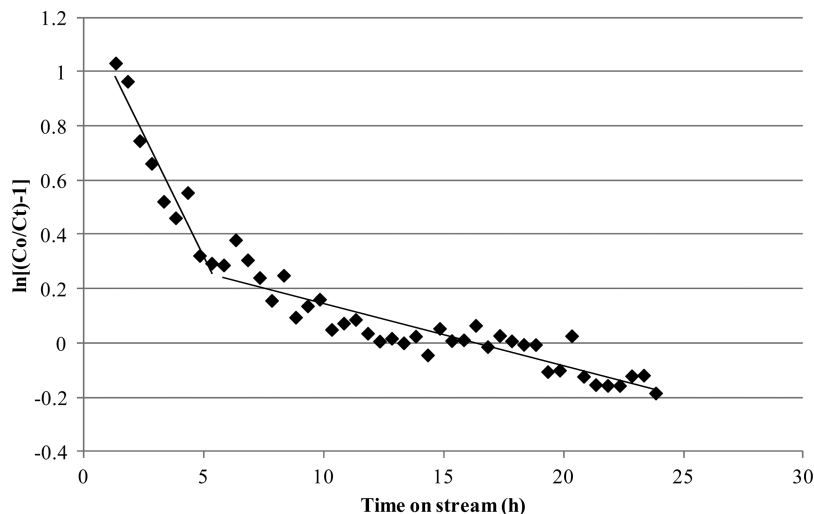
**Table 3. Hydrogen Sulfide Adsorption from a 1:1 H<sub>2</sub>S:H<sub>2</sub> Mix at 873 K**

catalyst	H <sub>2</sub> S adsorbed, $\mu\text{mol}\cdot\text{g}^{-1}$	H <sub>2</sub> :S(ads) <sup>b</sup>	Pt:S(ads) <sup>c</sup>
Pt/alumina	56.3	1:0.44	1:1.1
Pt/silica	51.6	1:0.25	1:1

<sup>b</sup>Ratio of hydrogen evolved to sulfur adsorbed. <sup>c</sup>Ratio of Pt to sulfur adsorbed.

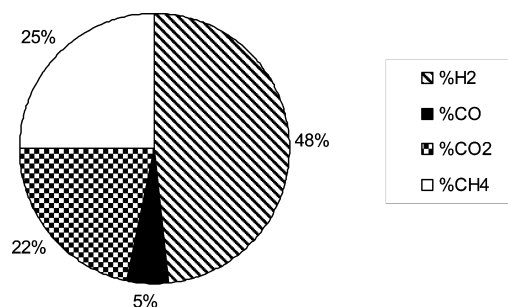
Given that this indicated that adsorption was dissociative, then an estimate of the amount adsorbed was calculated assuming  $2\text{CH}_3\text{SH} \rightarrow \text{CH}_3\text{S(ads)} + \text{H}_2$ . Using this assumption Pt/silica adsorbed  $53.2\ \mu\text{mol}\ \text{g}^{-1}$  giving a S:Pt ratio of 1, while Pt/alumina adsorbed  $33.6\ \mu\text{mol}\ \text{g}^{-1}$  giving a S:Pt ratio of 0.7.

**3.2. Reaction Studies.** The 0.2% Pt/alumina catalyst was tested under ethane steam reforming at 873 K as outlined in the Experimental Section. During the first 5 h carbon was being deposited on the catalyst surface as shown in Figure 1. After the

**Figure 1.** Carbon loss with time on stream.**Figure 2.** Deactivation rate constant plot over first 24 h.

first 5 h, the rate of carbon deposition was below detection limits but may have continued at a low rate. XRD analysis of the used catalyst revealed no bands identifiable as platinum metal, suggesting that no significant sintering had occurred. Nevertheless the activity decreased rapidly over the first 5 h and then more slowly over the next 24 h. The decrease in conversion with time was analyzed using  $\ln[C_t/(1 - C_t)] = -k_d t + \ln(k\tau_w)$ , where  $C_t$  is the conversion at time  $t$ ,  $k_d$  the deactivation rate constant, and  $\tau_w$  the weight time. The plot is shown in Figure 2.

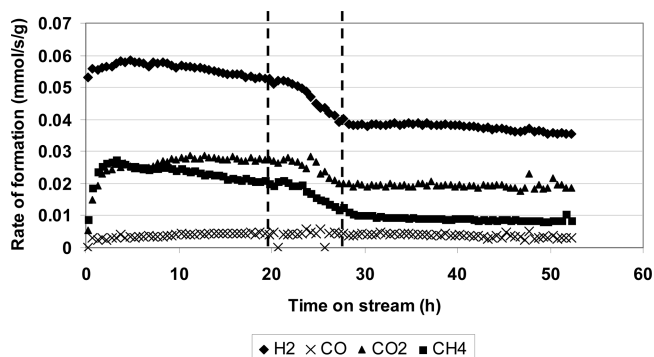
The plot shows two deactivation zones. The first related to the laydown of carbon with a deactivation constant of  $0.1819\ \text{h}^{-1}$ . The second zone shows a much slower deactivation with a deactivation constant of  $0.023\ \text{h}^{-1}$ . Figure 3 shows the molar selectivity obtained over the period of 5–24 h.

**Figure 3.** Molar product selectivity. Conditions: 873 K, 20 barg, 5:1 H<sub>2</sub>O:C<sub>2</sub>H<sub>6</sub>.

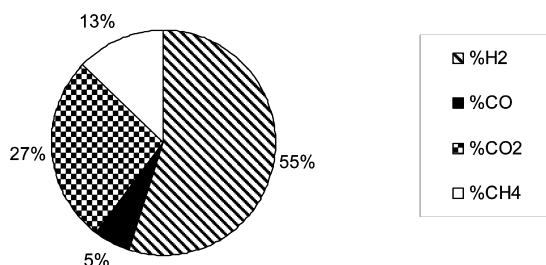
A fresh catalyst was run for 20 h and then 11.2 ppm hydrogen sulfide introduced. After 7 h the poison was removed from the feedstream and the feed reverted to pure ethane and steam. Figure 4 shows the effect of the H<sub>2</sub>S on the rate of formation of CO, CO<sub>2</sub>, H<sub>2</sub>, and CH<sub>4</sub>. Figure 5 shows the selectivity observed after the hydrogen sulfide has been removed. The selectivity to methane has dropped considerably. The conversion before addition of the hydrogen sulfide was  $\sim 40\%$ , whereas after removal of the poison it was  $\sim 17\%$ .

A fresh catalyst was run for 19 h and then methanethiol introduced at 11.2 ppm. After 4 h the poison was removed from the feedstream and the feed reverted to pure ethane and steam.



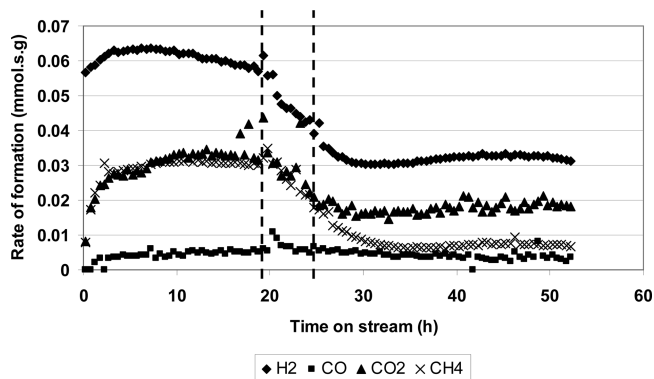


**Figure 4.** Effect of 11.2 ppm H<sub>2</sub>S on rates of formation (dotted lines show start and finish of addition, 7 h). Conditions: 873 K, 20 barg, 5:1 H<sub>2</sub>O:C<sub>2</sub>H<sub>6</sub>.

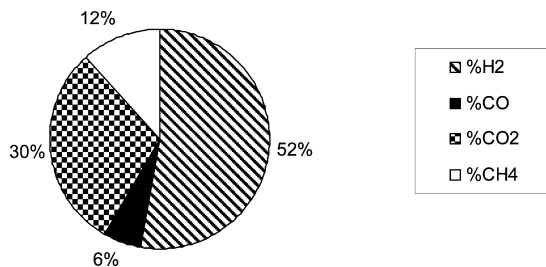


**Figure 5.** Molar product selectivity. Conditions: 873 K, 20 barg, 5:1 H<sub>2</sub>O:C<sub>2</sub>H<sub>6</sub> after H<sub>2</sub>S addition.

Figure 6 shows the effect of CH<sub>3</sub>SH on the rate of formation of CO, CO<sub>2</sub>, H<sub>2</sub>, and CH<sub>4</sub>. Figure 7 shows the selectivity observed



**Figure 6.** Effect of 11.2 ppm CH<sub>3</sub>SH on rate of formation (dotted lines show start and finish of addition, 4 h). Conditions: 873 K, 20 barg, 5:1 H<sub>2</sub>O:C<sub>2</sub>H<sub>6</sub>.



**Figure 7.** Molar product selectivity. Conditions: 873 K, 20 barg, 5:1 H<sub>2</sub>O:C<sub>2</sub>H<sub>6</sub> after CH<sub>3</sub>SH addition.

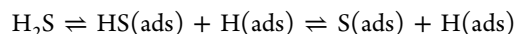
after the methanethiol has been removed. The selectivity to methane has dropped considerably. The conversion before addition of the methanethiol was ~40%; after the addition of methanethiol the conversion was ~6%.

#### 4. DISCUSSION

The adsorption of hydrogen sulfide and methanethiol on platinum has only been studied sparingly.<sup>10–13</sup> Nevertheless there is good agreement about what is expected from hydrogen sulfide adsorption at room temperature. Our value of 0.6:1 S:Pt is typical for sulfur adsorption on Pt/alumina.<sup>13–15</sup> The higher value (0.9) obtained for Pt/silica is also in keeping with the literature.<sup>13</sup> These values can be contrasted with carbon monoxide adsorption, which showed, as expected, catalysts with very high dispersion. The H<sub>2</sub>S and CO values over Pt/silica are very similar and, given a 1:1 ratio for CO:Pt,<sup>16</sup> suggest a 1:1 ratio for sulfur in line with other studies.<sup>13,17,18</sup> Over Pt/alumina the value was lower; however, care must be taken here as the amount adsorbed on the alumina has been subtracted. Nevertheless it is suggestive that the sulfur bonding is not identical over Pt/alumina and Pt/silica, which agrees with a study by Jackson et al.<sup>13</sup> where three types of adsorbed hydrogen sulfide were detected on Pt/alumina but only two types on Pt/silica. The H<sub>2</sub>:S(ads) ratio indicates that the surface species on both catalysts are a mix of S(ads) and SH(ads). This is in keeping with a high-temperature adsorption study, which used deuterium to determine the surface species.<sup>19</sup>

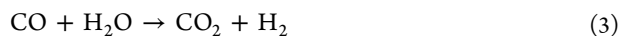
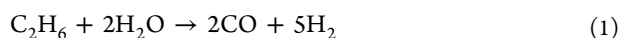
The adsorption of methanethiol has been studied even less than that of hydrogen sulfide especially over platinum. However, the adsorption of methanethiol has been studied over Pt(111),<sup>12</sup> and at 275 K the principal adsorbed state was identified as CH<sub>3</sub>S(ads). By measurement of the evolution of hydrogen formed from the dissociation of methanethiol, our adsorption results gave a S:Pt similar to that observed with hydrogen sulfide. In keeping with the hydrogen sulfide adsorption, Pt/silica gave a higher S:Pt ratio than Pt/alumina.

The adsorption of hydrogen sulfide at 873 K revealed a higher degree of dissociation and a S:Pt ratio of 1.3:1 for Pt/alumina and 1.6:1 for Pt/silica. Note that formation of the bulk sulfide (PtS<sub>2</sub>) is not thermodynamically favored at this temperature unless there is a standing concentration of hydrogen sulfide and the S:Pt ratios support this. When hydrogen was co-fed with H<sub>2</sub>S, the amount adsorbed decreased significantly (S:Pt ~ 1:1) and the main surface species is SH(ads) rather than S(ads). This is to be expected as we are now displacing the following equilibria to the left-hand side:



This is in agreement with the study<sup>19</sup> where deuterium was passed over a hydrogen sulfide saturated Pt/alumina catalyst at 873 K. Analysis of the small quantity of hydrogen sulfide desorbed indicated that the main species was HDS with only a small amount of D<sub>2</sub>S detected. So under steam reforming reaction conditions with excess hydrogen present, it would be expected that the sulfur species on the surface will be SH(ads) rather than S(ads). Therefore from the adsorption study it can be expected that there is the potential for a high S:Pt ratio under steam reforming conditions, that the support is likely to adsorb hydrogen sulfide, that the surface species is more likely to be SH(ads) rather than S(ads) due to the high hydrogen concentration, and that little of the sulfur adsorbed will be removed from the surface even after it has been removed from the feed.

The steam reforming of ethane can be described by the following equations:



Equation 1 represents steam reforming to produce CO and H<sub>2</sub> and subsequent water-gas shift (WGS, eq 3) allows the production of CO<sub>2</sub>, while methane can be formed by hydrogenolysis (eq 2). It is also possible to form methane via methanation;



The equilibrium percentages of hydrogen, methane, carbon monoxide, and carbon dioxide have been calculated on a dry gas basis for naphtha steam reforming at various temperatures and pressures.<sup>20</sup> Comparing the data in Figure 3 with the published data suggests that our system was operating close to equilibrium for the given pressure, temperature, and steam to carbon ratio.

Catalyst deactivation is a common problem in steam reforming; however, at a steam to carbon ratio of 2.5 it was not expected that there would be significant carbon deposition; nevertheless Figure 1 shows that during the first 5 h on-stream there was significant carbon deposition and associated with this was a period of rapid deactivation (Figure 2). Because the start-up procedure has steam present before ethane is fed, it is unlikely that carbon deposition was due to a transient low steam to carbon ratio. Thermodynamics would suggest that there should not be carbon deposition at the steam to carbon ratio used,<sup>20</sup> but this calculation is very dependent upon the form of carbon assumed on the surface and the enthalpy and entropy associated with it. Given the short-term nature of the carbon deposition, it is likely that the deposition was associated with high-energy sites on the surface (with different thermodynamic parameters), and once these were deactivated the system represents that described by the general thermodynamics. The loss in activity during the period of carbon laydown was not unexpected; however, after this initial non-steady-state behavior the rate of catalyst deactivation decreased by over an order of magnitude. Over the rest of the time on stream no carbon deposition was detected. Hence the continued deactivation may be due to sintering or very low level carbon deposition.

The addition of hydrogen sulfide or methanethiol resulted in a significant loss in activity of the catalyst. The overall conversion was approximately halved during the period of sulfur addition from hydrogen sulfide, while it was reduced by over 75% when methanethiol was added. Most of the loss in activity can be directly related to site blocking by adsorbed sulfur; however, in a study of hydrogen sulfide poisoning over a Pt/alumina catalyst<sup>21</sup> it was shown that the adsorbed sulfur not only causes site blocking but may also cause sintering of the Pt crystallites. Any such sintering will also result in a reduction in activity. It is possible to be more detailed and examine the effect of the sulfur on the specific reactions that are occurring during steam reforming. These include the water-gas shift reaction and methane forming reactions, namely, hydrogenolysis and methanation. From the change in selectivity (Figures 3, 5, and 7) it is clear that not all reactions were affected to the same extent by the presence of the poisons. Indeed the selectivity to

hydrogen was enhanced by the addition of the sulfur poison, with hydrogen sulfide giving a selectivity increase of 7%. This enhancement was maintained after the sulfur was removed from the feedstream. To examine the effect on each product in more detail a pseudo-first-order deactivation rate constant was determined for each product during the period when the sulfur was introduced. Table 4 shows the deactivation rate constants

**Table 4. Deactivation Rate Constants ( $\times 10^{-4} \text{ min}^{-1}$ ) Obtained for Each Product When H<sub>2</sub>S and CH<sub>3</sub>SH Are Introduced in to the Feedstream**

product	poison added	
	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

obtained from the deactivation of each of the gaseous products formed when hydrogen sulfide and methanethiol were introduced into the system.

It is clear that methanethiol was more deleterious than hydrogen sulfide. This may be related to the potential for methanethiol to deposit carbon (from the methyl fragment) as well as sulfur.<sup>12</sup> It is also clear that the rate of deactivation of the products is not the same. The formation of methane was most affected, deactivating at almost double the rate of the other products no matter whether hydrogen sulfide or methanethiol was the poison. This effect is not surprising given that the formation of methane requires a larger ensemble size than steam reforming or water-gas shift reaction. Over nickel catalysts Rostrup-Nielsen<sup>5</sup> found steam reforming to involve ensembles of three to four nickel atoms, while the formation of methane required six or seven atoms.<sup>5,22</sup> Methane can be formed either by methanation ( $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$ ) or hydrogenolysis of ethane ( $\text{C}_2\text{H}_6 + \text{H}_2 \rightarrow 2\text{CH}_4$ ). At lower temperatures and at these pressures methanation is not favored over platinum;<sup>23</sup> rather methanol is formed. Similarly platinum catalysts have been shown to be relatively ineffective for hydrogenolysis compared to other group VIII metals, e.g., osmium.<sup>24</sup> However, at 873 K even if methanol was formed, it would be rapidly decomposed or react with steam to give carbon monoxide and hydrogen,<sup>25,26</sup> while alkanes easily fracture to C-1 species.<sup>19,27–29</sup> Mechanistically both reactions proceed through an adsorbed C-1 species and its subsequent hydrogenation to methane;<sup>23,30</sup> therefore, if sulfur disrupts this process, a decrease in methane formation will be seen. Such behavior has been seen with sulfur poisoning of propane dehydrogenation over Pt/Al<sub>2</sub>O<sub>3</sub>,<sup>19</sup> where cracking to methane was inhibited in favor of dehydrogenation to propene. Note that by inhibiting methane formation the hydrogen content of the effluent gas will increase as both hydrogenolysis and methanation use hydrogen to form methane.

Hydrogen and carbon dioxide exhibit very similar deactivation rate constants, both when hydrogen sulfide or methanethiol is the poison, which suggests the deactivation of these products is linked. Although in principle carbon dioxide could be a primary product ( $\text{C}_2\text{H}_6 + 4\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 7\text{H}_2$ ), it is more likely that the primary reaction is to form carbon monoxide ( $\text{C}_2\text{H}_6 + 2\text{H}_2\text{O} \rightarrow 2\text{CO} + 5\text{H}_2$ ), which then rapidly reacts with steam to give carbon dioxide and hydrogen via the water-gas shift reaction. With use of this reaction sequence, over half the

hydrogen produced and all of the carbon dioxide would come via WGS. There have been few studies on the effect of sulfur on the WGS reaction over platinum, but a recent study<sup>31</sup> over a Pt/ceria catalyst showed that the addition of hydrogen sulfide reduced activity by a strong interaction with the ceria support rather than the platinum. Our adsorption study and that of others<sup>14</sup> confirm that hydrogen sulfide does adsorb on alumina and so may affect the WGS reaction in a manner similar to that found with ceria, although the differences in the chemistry between the two supports would make this unlikely; however, even if that was not the case, any effect on the WGS reaction would be seen in the yields of both hydrogen and carbon dioxide.

The product exhibiting the least amount of deactivation was carbon monoxide. This would suggest that the steam reforming reaction is the reaction least affected by sulfur poisoning; however, conversion in both systems decreased significantly, so it is more likely that the absence of significant deactivation with respect to carbon monoxide is a result of the differential between the steam reforming and WGS reactions. If the WGS reaction is inhibited, then the amount of carbon monoxide should increase; however, this will be offset by a general decrease in conversion. The combination of these factors may result in a carbon monoxide yield that is apparently not affected significantly by sulfur poisoning.

In a recent study over a nickel catalyst at 1073 K, sulfur poisoning appears to significantly enhance carbon deposition<sup>32</sup> during steam reforming. However, this result is out of keeping with most other studies which indicate that sulfur inhibits carbon deposition.<sup>5,22,33</sup> Indeed over the Pt/alumina catalyst analysis during the period of sulfur poisoning revealed no carbon laydown in keeping with the behavior in the absence of sulfur. It has been shown that, over platinum, sulfur will inhibit the Boudouard reaction ( $2\text{CO} \rightarrow \text{CO}_2 + \text{C}$ )<sup>10,34</sup> and reduce deposition of carbon from alkane dehydrogenation ( $\text{C}_n\text{H}_{2n+2} \rightarrow n\text{C} + (n+1)\text{H}_2$ ).<sup>19</sup> As these are two of the main routes to carbon deposition in steam reforming, the absence of carbon laydown over platinum when sulfur is present is in keeping with these studies.

When methanethiol is removed, there was a slight (~10%) recovery in activity for hydrogen, carbon dioxide, and methane production. The rate of formation of carbon monoxide did not appear to change; however, a 10% increase in rate at these low levels would be within the variability observed in the system. This slight recovery for the methanethiol poisoned system may relate to removal of carbon deposited from the methanethiol rather than removal of any sulfur.<sup>12</sup> However when hydrogen sulfide was removed from the feedstream, there was no obvious regeneration, with the rate of formation of all products remaining essentially constant at the new lower levels. This behavior was expected from the adsorption studies and from studies where sulfided platinum catalysts have been subjected to hydrogen at 873 K.<sup>17</sup> Even in the presence of hydrogen, sulfur is not easily removed from a platinum surface at 873 K. The adsorption studies indicate that a PtSH species is formed at 873 K in the presence of hydrogen. However, the catalyst was still deactivating when the poison feed was removed revealing that a steady state had not been reached, which would imply that full saturation of the platinum had not occurred. The most obvious reason for this is that because the support can act as a large sulfur sink, most of the sulfur is adsorbed on the alumina and not the platinum. However the amount of sulfur passed over the catalyst would have saturated the support and

also the evidence from the adsorption study is that adsorption takes place on metal and support simultaneously. Therefore we must look for another explanation, and it is possible that the poisoning resistance is due to the initial carbon laydown. The sulfur is not adsorbing on a clean platinum surface but on one which has had carbon deposited, and, hence, effects like sintering and surface reconstruction may be inhibited: this has been proposed previously for reactions over Ni and Ru catalysts.<sup>33</sup> A second plausible explanation for the slow deactivation is that the sulfided catalyst has some activity in its own right. Sulfided platinum catalysts are active for hydrodesulfurization and hydrogenation;<sup>35,36</sup> hence, it is not inconceivable that the sulfided platinum surface retains some activity for steam reforming.

## 5. CONCLUSION

In this study we have examined the adsorption of hydrogen sulfide and methanethiol over platinum catalysts and examined the effect of these poisons on the steam reforming of ethane. The adsorption study revealed that in the absence of hydrogen the adsorbed state of sulfur at 873 K was S with the formation of a substoichiometric sulfide, PtS<sub>1.3</sub>. At 873 K in the presence of hydrogen, however, the adsorbed state of hydrogen sulfide was SH, rather than S, and the Pt:S ratio was reduced to unity. This behavior, taken with thermodynamic stability, suggests that at higher temperatures the effect of sulfur may be lessened as the amount of adsorbed sulfur decreases. At a level of 11.2 ppm, both hydrogen sulfide and methanethiol deactivated the catalyst over a number of hours but methanethiol was significantly more deleterious, reducing the conversion by almost an order of magnitude, probably caused by the co-deposition of sulfur and carbon. The potential for carbon deposition as well as sulfur from R-SH species means that the R-group as well as the sulfur must be considered when assessing the likely deleterious effect of an R-SH molecule. As expected no carbon laydown was detected during sulfur poisoning. Analysis of the product distribution revealed that the effect of sulfur was not uniform on the reactions occurring, with the production of methane reduced proportionally more than the other products, due to the surface sensitivity of the hydrogenolysis and methanation reactions. The WGS reaction was affected to a lesser extent. No regeneration was observed when hydrogen sulfide was removed from the feedstream in agreement with adsorption studies. A slight regeneration was observed when methanethiol was removed from the feed, but this was believed to be due to the removal of carbon rather than sulfur. The overall effect of sulfur poisoning was to reduce activity but enhance hydrogen selectivity by differential poisoning of the reactions that consume hydrogen.

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### Notes

The authors declare no competing financial interest.

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