REACTION PATHWAYS FOR CLAUS TAIL GAS REDUCTION CATALYSTS: RELEVANCE TO FIELD OPERATIONS AND INDUSTRIAL PRACTICE

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Summary

The objective of the research described in this paper was to ascertain reaction pathways for reduction of sulfur species in catalytic tail gas treatment units. The results of these studies indicate that the chemistry may be somewhat different to generally assumed mechanisms, at least generally assumed by these authors.

It has been found that SO_2 reduction to H_2S occurs, as assumed, by reaction with H_2 and by reduction of sulfur formed as an intermediate in the Claus reaction. Both alumina and molybdenum-based sites are capable of promoting the Claus reaction. Catalyst pre-activation with H_2/H_2S mixtures is required to obtain maximum CO water gas shift reactivity, a vital source of reducing potential in tail gas reduction. CS_2 conversion occurs at MoS_2 reduction sites by hydrogenation and, perhaps by hydrolysis at the same sites. The same pathways exist for COS but, also, it may be formed by interaction of H_2S with the surface intermediate of the water gas shift reaction leading to net formation of COS at low temperatures (< 240°C). Conversion of CS_2 and COS by hydrolysis on alumina sites may be very slow at temperatures < 275°C. The catalyst used in this study lead to formation of methyl mercaptan when CS_2 was present in the feed gas. Removal of CS_2 from the feed gas greatly decreased the production of methyl mercaptan. However, since mercaptan formation was not eliminated completely, it seems that it can also be formed by hydrogenation of COS or the thio-intermediate produced during the WGSR.

Although no experiments were conducted < 300°C to study the effect of hydrocarbons on Claus tail gas reduction catalysts, reactive hydrocarbons such as toluene and xylene lead to carsul accumulation on the catalyst at 300°C, a matter likely related to the intermediate formation of sulfur during SO_2 reduction.

Advisory: All comments and conclusions made in this paper relate to a commercial alumina Co-Mo product. The same observations may, or may not, be seen with other commercial catalysts.

Despite the complexity and cost of treatment of Claus tail gas by catalytic reduction and recycle of H_2S, this process remains the only method which can be applied to achieve > 99.9 % sulfur recovery in a large scale plant. As such, it has become the preferred technology in the USA and is applied wherever > 99.9 % efficiency is mandated.

The heart of a Claus tail gas reduction system is the catalytic hydrogenation reactor (Figure 1), which reduces SO_2 and S_x vapour species to H_2S over an alumina based CoS-MoS_2 catalyst. As will be described, this catalyst also carries out several other vital functions. The purpose of this paper is to describe the reaction pathways and mechanistic features of the surface reactions illustrating how they contribute to the overall process and affect the operation of a commercial unit. Before this analysis is presented a brief overview of the entire tail gas treatment system will be given.

Figure 1
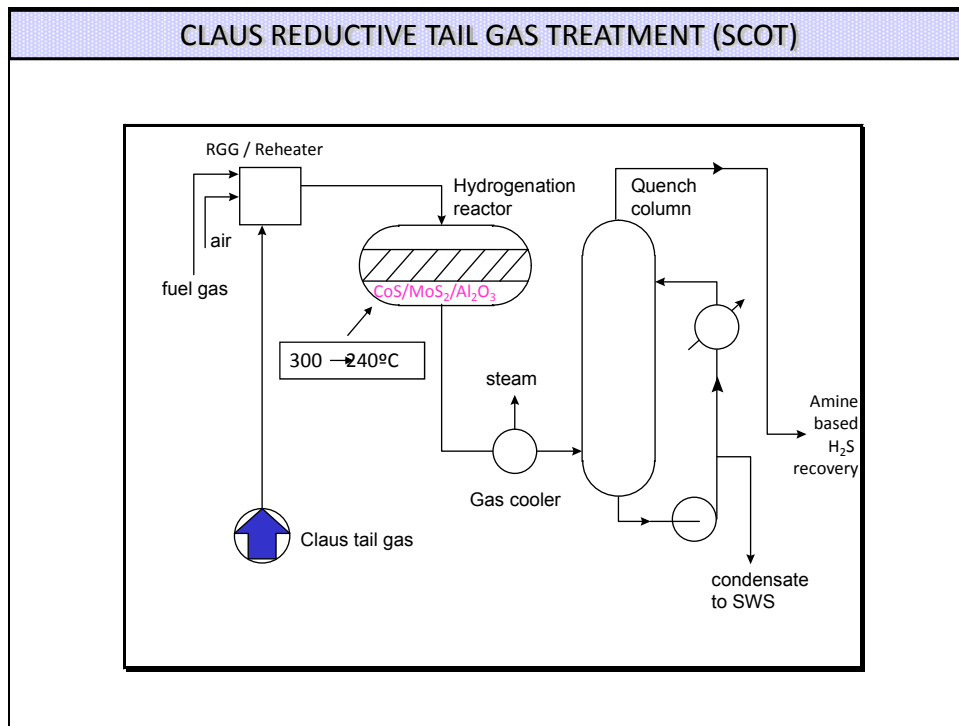
Usually, the hydrogenation reactor receives process gas from the second Claus catalytic condenser and, so, treats a gas mixture which contains H_2S, SO_2, S_x vapour species and lesser amounts of CS_2 and COS as the sulfur-containing components. In addition to N_2 and H_2O, CO and H_2 will be present, the amounts being dependent on the feed acid gas composition and the operating conditions of the Claus furnace. In its original form, a catalytic reduction process (CRP) utilized a reducing gas generator (RGG, Figure 1) which served the dual purpose of providing supplemental CO and H_2 as well as re-

heating the gas to around 300°C, the temperature at which original catalyst formulations demonstrated optimum activity. Since the RGG operates in sub-stoichiometric mode it is important to work within CH_4/O_2 ratios which do not produce solid carbon and also to use clean CH_4 fuel gas. Use of refinery gas which contains larger alkanes and aromatic hydrocarbons leads quickly to catalyst fouling and, subsequently, reduced efficiency of the hydrogenation unit.

Newer catalyst preparations have been designed to operate effectively at 220 – 240°C allowing the RGG – heater to be removed. This innovation is possible because, in most plants, the process gas contains sufficient CO and H_2 to achieve reduction of the sulfur species. In this adaptation, process gas re-heat can be achieved using indirect methods so mitigating, in part, the oft-used criticism that CRP plants are energy and carbon inefficient. Indeed, according to some estimates, 4 moles of CO_2 result for every SO_2 reduced for a plant operating with RGG – heaters and hydrogenation units at 300°C. Despite the catalyst improvements and reduction of hydrogenation unit temperature to 220 – 240°C, CRP is complex because the water quench system handles large volumes of sour water and H_2S recovery requires treatment of low pressure gas with specially formulated MDEA-based solvents. However, the reader will appreciate that by definition, > 99.9 % sulfur recovery cannot be achieved without sophisticated technology, which, as a consequence, will always have a high energy demand. The absence of simpler competing > 99.9 % processes for large scale plants underlines this point.

Overview of Catalytic Functions

A tail gas reduction catalyst, as produced by the catalyst manufacturer, consists of CoO and MoO_3 deposited on γ-Al_2O_3. This material must be activated before use by treatment with H_2 and H_2S, a process which results in formation of CoS and MoS_2. Activation conditions provided by the manufacturer must be followed carefully to avoid reduction of MoO_3 to metallic Mo, an inactive species. Some companies provide activated catalyst directly to the plant.

The role of the CoS is not known with certainty and generally is described as a promoter but the MoS_2 sites are thought to be the center for SO_2 and S_x vapour reduction and shift of CO to H_2 via the water gas shift reaction (WGSR) (Figure 2). H_2 might be activated by oxidative addition to a Mo=S bond or be available via intermediates formed through the dynamic equilibrium of the WGSR. The role of the WGSR will be discussed in detail with respect to COS and CH_3SH formation but, also, it should be recognized that shift of CO to H_2 is, in itself, a very important process as it limits emission of CO from the plant and reduces CH_4 requirements in the thermal incinerator.

Figure 2
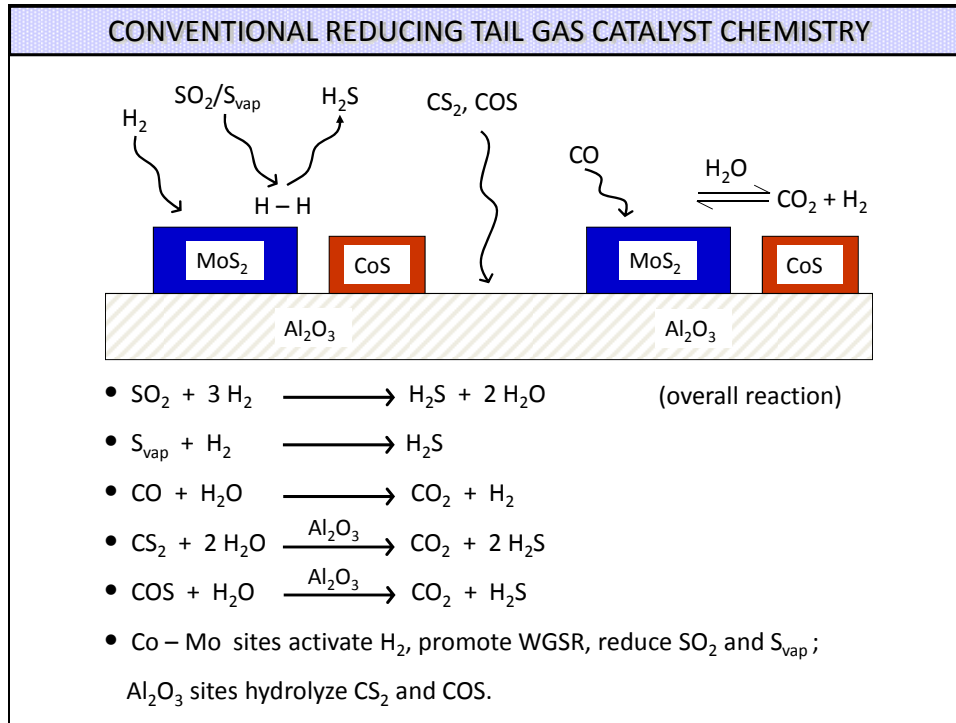
Generally, it is assumed that CS_2 and COS are hydrolyzed by H_2O on alumina sites (Figure 2). This suggestion seems reasonable given that alumina is the bulk support and water may be up to 40 mole % of Claus tail gas. Undoubtedly, hydrolysis of these compounds must occur to some extent but, as will be described later in this paper, hydrogenation of these compounds also occurs at metal sulfide sites, sometimes with unwanted consequences. Particularly, hydrolysis of CS_2 and COS in low temperature catalytic units is questionable as rates of these reactions are known to be slow $< 275°C$.

Part of this investigation has examined the actual mechanism for SO_2 conversion, especially for low temperature applications. Previously, it has been assumed that SO_2 is reduced to H_2S by H_2. But, since γ-Al_2O_3 promotes the Claus reaction (Figure 3), why then can SO_2 conversion not occur sequentially by first reduction with H_2S to sulfur at alumina sites followed by further reduction of the sulfur vapour by H_2 on sulfide sites? The ramification of this possibility on the overall mechanism is considered in the following section.

How is SO_2 Converted over Tail Gas Reduction Catalyst?

The work reported in this article used a commercial catalyst but not one specifically designed for low temperature operation. Although this catalyst is likely to demonstrate

the same general pattern of activity, the reader should not assume that all commercial catalysts will behave in the same manner. The reaction pathways depicted in Figure 3 illustrate that elemental sulfur might be formed either via the Claus reaction between H_2S and SO_2 or by reduction of SO_2 with H_2. Our laboratory experiments confirmed that sulfur was formed although it was only observed when the reaction temperature was < 240°C. Above this temperature, no sulfur could be collected so we can assume that if sulfur is an initial product at higher temperatures, sulfur hydrogenation to H_2S is a rapid reaction on $CoS-MoS_2$ promoted alumina above 240°C. Restricting the discussion to production of sulfur by the Claus reaction for the moment, the question also arises as to whether the sulfur is formed at alumina sites or on $CoS-MoS_2$ sites. Obviously, we know that the Claus reaction occurs over alumina. In a separate series of experiments, the Claus reaction was investigated over another ASRL-prepared $CoS-MoS_2$ alumina catalyst in which sufficient Co and Mo-species were added to cover the entire alumina surface. These experiments used a feed gas which contained only N_2, H_2O, H_2S and SO_2 (no H_2) with the observation that the Claus reaction proceeded readily over the $CoS-MoS_2$ surface. These results suggest that even more complex reaction pathways for conversion of SO_2 are possible in which sulfur may be formed by the Claus reaction at either alumina or $CoS-MoS_2$ sites followed by reduction of the sulfur to H_2S with H_2 at $CoS-MoS_2$ sites.

Figure 3

HOW IS SO_2 REDUCED OVER TAIL GAS REDUCTION CATALYSTS?

SO_2 $S_8 + H_2O$ $2H_2S + SO_2 \rightleftharpoons \frac{3}{8}S_8 + 2H_2O$ H_2S

$H - H$ $H - H$

| MoS$_2$ | CoS | MoS$_2$ | CoS |

Al_2O_3 Al_2O_3

- Since TGRC contain Al_2O_3, they should promote the Claus reaction:

  $2 H_2S + SO_2 \rightleftharpoons \frac{3}{8} S_8 + 2 H_2O$

- SO_2 reduction by H_2 on Co – Mo sites to form sulfur is also possible:

  $2 H_2 + SO_2 \longrightarrow \frac{1}{8} S_8 + 2 H_2O$

  WHAT EVIDENCE DO WE HAVE FOR THE MECHANISM?

- ASRL observation: < ~ 240°C, S_8 can be observed as a product.
- Look at H_2S in product: ≥ 240°C net formation

  vs 200°C H_2S conversion

Analysis of the data sets in Table 1 and summarised in Figure 4 confirm that below 240°C, SO_2 conversion to sulfur occurs to some extent by the Claus reaction as insufficient H_2 and CO were consumed, and a net conversion of H_2S was observed, at the 200°C temperature to account for the observed SO_2 consumption. The analysis presented in Figure 4 suggests that at 200°C, 38% of the SO_3 was reduced by the Claus reaction and 48% via reduction of SO_2 by H_2 to produce elemental sulfur.

This is all very interesting but what is the commercial relevance? One, regardless of exact reaction mechanisms, is that at some temperature, likely below 240°C, elemental sulfur could be produced in a CRP so providing a mechanism for appearance of solid sulfur in the quench water, other than the "usual" SO_2 breakthrough explanation. Catalyst activity will, of course, be an important parameter controlling the appearance of elemental sulfur in the product gas.

COS, CS_2 and CO Conversion Over Tail Gas Reduction Catalysts

Again, the reader is reminded that the data presented here are specific to the commercial catalyst chosen for the study. However, quite possibly, other catalysts will show the same general trends but at different temperatures and according to their general activity, a matter related to time on-stream. This suggestion is made on the basis that the chemistry of the active sites cannot vary substantially since most commercial catalysts are based on alumina, CoS and MoS_2, but the rates of the individual reactions will change according to the catalyst preparation so affecting the final product composition. As will be seen in the following sections, COS is both destroyed and formed over Claus TG reduction catalysts and both processes are tied to a complex network of chemical reactions.

The first matter to be aware of from the data presented in Figure 5 is that the COS "conversion" scale ranges from negative to positive. At 300°C, 70 - 75 % COS conversion was observed, but at 240 and 200°C, product COS levels exceeded feed input amounts. As may be noted from Figure 5, catalyst activity took some time to stabilize after reduction in process temperature but net COS formation was ca. 130% at 200 and 240°C after 8 hours on-line at the new temperature. Clearly, COS formation on a tail gas reduction catalyst could have a significant affect on total sulfur recovery in the plant.

How can these results be explained? If it assumed, for the moment, that all COS chemistry occurs at alumina sites, hydrolysis of COS can be advanced to explain its consumption and reaction of H_2S with CO_2 offer a pathway by which it might be formed. These reactions are linked together in the following equilibrium process.

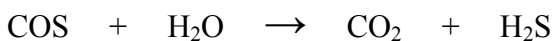$$COS \quad + \quad H_2O \quad \rightarrow \quad CO_2 \quad + \quad H_2S$$

Table 1

Experimental Data and Calculated Conversions for the Co/Mo-Based Tail Gas Reduction Catalyst at 200 – 300°C and Space Velocity of 2000 h^{-1} – Full Feed

DRY FEED (saturated with 22% H2O)[#]

	% N2	% CO2	% H2S	% COS	% SO2	% CO	%H2	% CS2	MeSH		H2S:SO2
	72.15	23.09	0.755	0.064	0.378	1.51	1.92	0.028	–		2.00

				SAMPLE							Conversion			
Time(hrs): (300C)				(ppmv)	(ppmv)			(ppmv)	(ppmv)		% SO2	% CS2	% COS	% CO
1.0	72.15	24.81	1.73	153	28	0.131	2.01	3.7	27		99.3	98.7	76.1	91.3
2.0	72.15	25.66	1.74	172	14	0.153	2.22	2.3	27		99.6	99.2	73.2	89.9
4.0	72.15	26.08	1.83	176	14	0.145	2.24	2.8	29		99.6	99.0	72.4	90.4
6.0	72.15	24.89	1.75	168	12	0.153	2.14	2.5	29		99.7	99.1	73.7	89.9
8.0	72.15	24.95	1.78	165	13	0.150	2.25	2.6	28		99.7	99.1	74.1	90.1
(240C)														
9.0	72.15	24.49	1.63	549	18	0.481	1.90	29	83		99.5	89.6	14.3	68.2
10.0	72.15	25.48	1.75	817	20	0.493	1.86	52	71		99.5	81.3	−27.6	67.3
12.0	72.15	24.60	1.68	1300	27	0.533	1.67	81	53		99.3	71.3	−103.0	64.7
14.0	72.15	24.68	1.66	1363	32	0.532	1.70	86	45		99.2	69.4	−113.0	64.8
16.0	72.15	24.72	1.60	1494	35	0.540	1.64	90	44		99.1	67.9	−133.4	64.2
(200C)														
17.0	72.15	24.12	0.82	2497	157	1.041	1.75	167	26		95.9	40.6	−290.2	31.1
18.0	72.15	23.67	0.68	2231	288	1.162	1.61	182	7.1		92.4	35.2	−248.5	23.1
20.0	72.15	23.38	0.52	1652	437	1.284	1.58	193	3.1		88.4	31.3	−158.1	15.0
22.0	72.15	23.55	0.48	1557	498	1.321	1.65	202	3.3		86.8	28.8	−143.4	12.5
24.0	72.15	23.24	0.45	1492	525	1.321	1.62	194	1.8		86.1	31.0	−133.1	12.5

Feed and product analyses reported on a dry & sulfur-free basis

[#] Wet feed composition also contained 800 ppmv of sulfur vapour (as S8).

Figure 4

EVIDENCE FOR CLAUS REACTION OVER TGR CATALYST

72.2% N_2, 23.1% CO_2, 0.76% H_2S, 0.38% SO_2, 0.06% COS, 0.03% CS_2, 1.5% CO, 1.9% H_2, 0.08% S_8, 22% H_2O

[Chart: % SO_2 Conversion vs Time on Stream (h)]

300°C **240°C** **200°C** 86%

Feed H_2S (mol%):	*0.76*	*0.76*	*0.76*
Prod H_2S (mol%):	*1.77*	*1.65*	*0.47*

38%

net H_2S formation vs H_2S conversion

a) $2H_2 + SO_2 \rightarrow \frac{1}{8}S_8 + 2H_2O$ $2H_2 + SO_2 \rightarrow \frac{1}{8}S_8 + 2H_2O$ 48%

b) $H_2 + \frac{1}{8}S_8 \rightarrow H_2S$ $2H_2S + SO_2 \rightarrow \frac{3}{8}S_8 + 2H_2O$ 38%

a + b) $3H_2 + SO_2 \rightarrow H_2S + 2H_2O$

➢ if Claus reaction alone at 200°C expect SO_2 conversion of 57% (vs 86% exptly)

$$2H_2 + SO_2 \longrightarrow \frac{1}{8}S_8 + 2H_2O$$

➢ predict H_2S conversion of 34% if take SO_2 reduction by H_2 into account (vs 38%)

Figure 5

COS CONVERSION BEHAVIOUR OVER TGR CATALYST

72.2% N_2, 23.1% CO_2, 0.76% H_2S, 0.38% SO_2, 0.06% COS, 0.03% CS_2, 1.5% CO, 1.9% H_2, 0.08% S_8, 22% H_2O

[Chart: % COS Conversion vs Time on Stream (h)]

300°C

COS conversion

240°C

200°C

net COS formation at 240 and 200°C

➢ COS exhibits a complex formation / conversion behaviour as a function of temperature

➢ COS formation at 240 – 200°C corresponds to ~0.1% in product
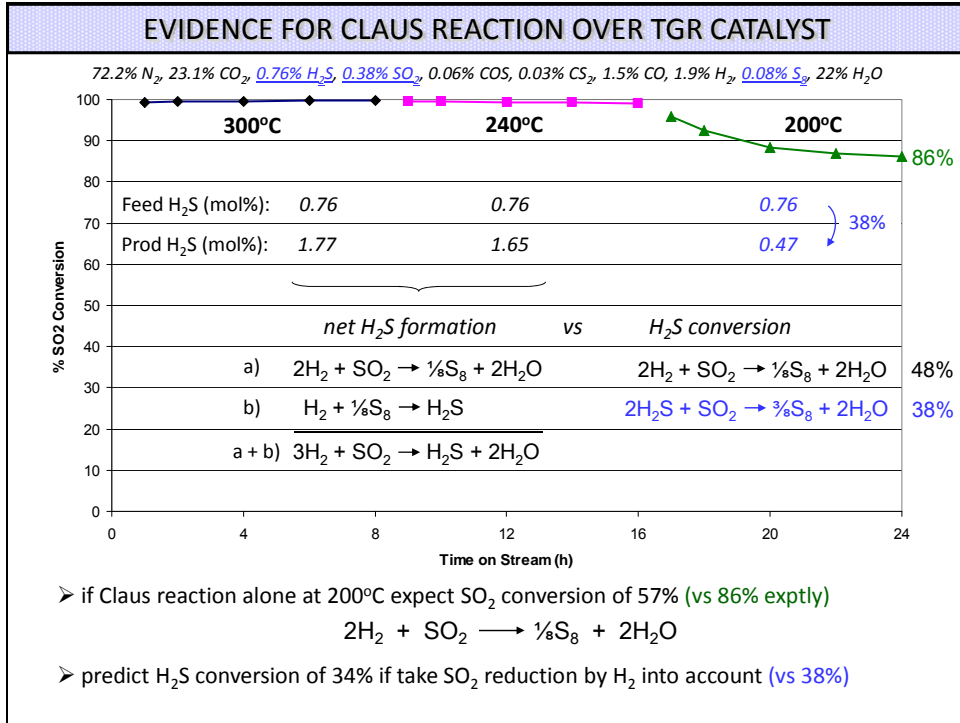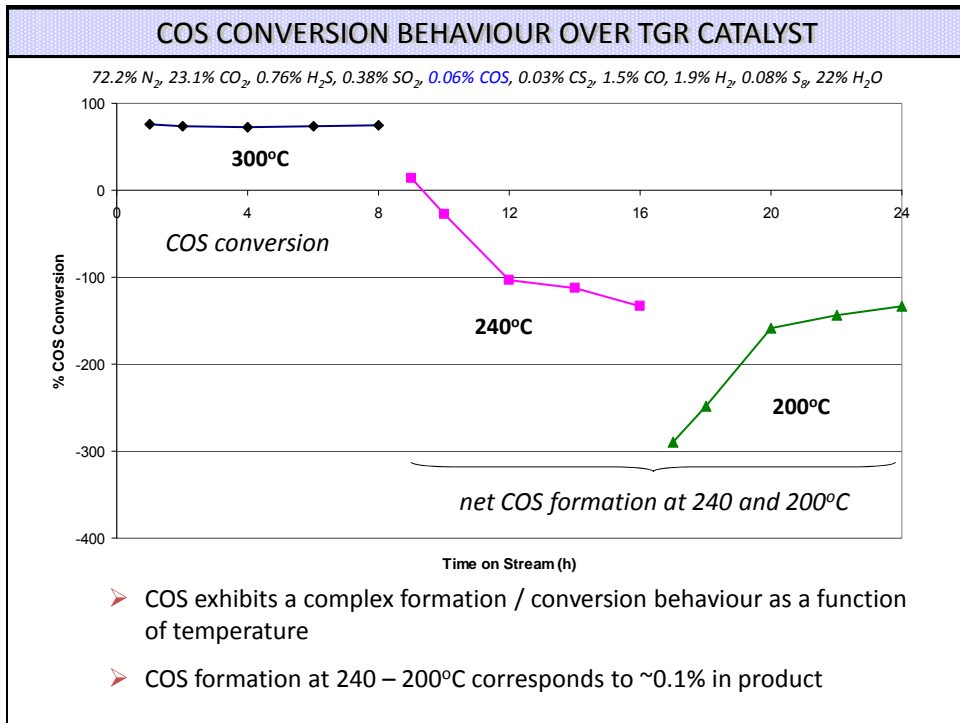
In other words, the amount of COS seen as a function of temperature is simply controlled by the equilibrium of these species. As may be seen from Table 2a, equilibrium conversion predictions for COS do not match the experimental observations (Table 1), particularly at 200 and 240°C. Indeed, at 200 and 240°C, net production of COS was observed (+ 130 %) instead of the predicted conversion of > 98 %. Even at 300°C, the observed conversion of COS (ca. 74 %), is considerably lower than the predicted value (97.5 %). Clearly, for the catalyst used in this study, pathways for conversion of COS are kinetically limited, an observation not entirely unexpected if COS destruction is to take place only by hydrolysis on alumina sites.

As mentioned earlier, CO shift via the WGSR is a very important function of Claus tail gas reduction catalysis as it provides supplemental H_2 for overall conversion of sulfur species to H_2S. A very simplified mechanism for the shift reaction (Figure 6) shows formic acid as a surface intermediate, a species which, of course, can be attained on the catalyst surface either from CO/H_2O or from CO_2/H_2. Since it known that alumina is a very poor WGSR catalyst, it can be assumed that this reaction proceeds over MoS_2 surface sites, perhaps with CoS promoting the process in some way. The "formic acid" surface species is really an activated form of H_2 so it is conceivable that SO_2 and S_x reduction might occur via these intermediates. Furthermore, COS may also be formed by reaction of H_2S with the "formic acid" intermediate in the sour gas shift reaction (SGSR, Figure 6), complicating the analysis for the net formation of COS at lower temperatures. The picture for COS formation and conversion is actually even more complicated as CS_2 produces COS as an intermediate via its hydrolysis, if, indeed, this reaction actually occurs in a CRP catalytic unit. Thus, it may be seen (Table 1) that while CS_2 conversion is > 99 % at 300°C, COS conversion is only 74 %, possibly reflecting incomplete conversion of COS formed by the hydrolysis of CS_2. An overview of COS formation and conversion mechanisms is given in Figure 7. Overall, COS levels in the product gas leaving a CRP hydrogenation unit depends on concentrations of many species (COS, CS_2, CO, H_2O, H_2, CO_2 and H_2S), the rates of the several processes (Figure 7), which, in turn, depend on catalyst activity and the temperature at which the unit is operating.

As may be seen by comparison of the equilibrium predictions for CO conversion (Table 2a) to actual data (Table 1), the WGSR is kinetically limited over this catalyst at 200 and 240°C. These observations are not surprising as the catalyst was not designed for low temperature operation.

Table 2a

Calculated Equilibrium Composition and Conversions for the Full Tail-Gas
Feed at 200° - 300°C

DRY FEED (saturated with 22% H2O)[#]

% N2	% CO2	% H2S	% COS	% SO2	% CO	%H2	% CS2	% CH3SH	H2S:SO2
72.15	23.09	0.755	0.064	0.378	1.51	1.92	0.028	-	2.00

Temp (oC):	EQUILIBRIUM			(ppmv)	(ppmv)			(ppmv)	(ppmv)	Conversion			
										% SO2	% CS2	% COS	% CO
300	72.15	24.66	2.08	16.3	0.0	0.0326	1.45	0.0	0.0	100.0	100.0	97.5	97.8
240	72.15	24.67	2.08	8.1	0.0	0.0124	1.47	0.0	0.1	100.0	100.0	98.7	99.2
200	72.15	24.69	2.08	4.1	0.0	0.0056	1.47	0.0	0.9	100.0	100.0	99.4	99.6

Feed and equilibrium compositions reported on a dry & sulfur-free basis

[#] Wet feed composition also contained 800 ppmv of sulfur vapour (as S8).

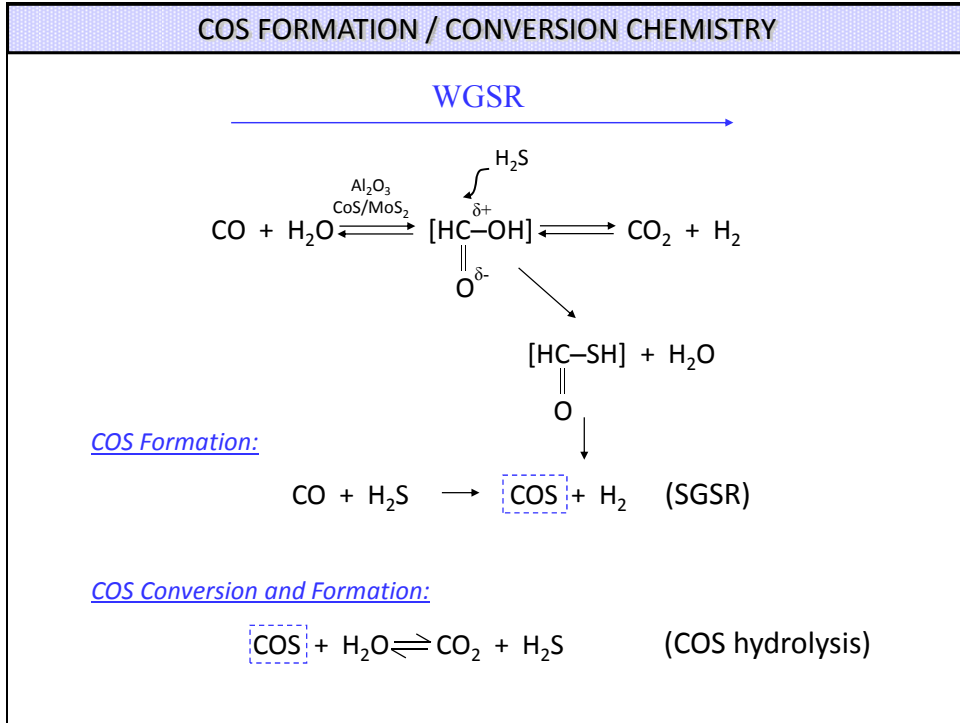## Table 2b

Calculated Equilibrium Composition and Conversions for the Tail-Gas
Feed Without CS$_2$ at 200° - 300°C

DRY FEED (saturated with 22% H2O)[#]

% N2	% CO2	% H2S	% COS	% SO2	% CO	%H2	% CS2	% CH3SH	H2S:SO2
72.18	23.09	0.755	0.064	0.378	1.51	1.92	-	-	2.00

Temp (oC):	EQUILIBRIUM			(ppmv)	(ppmv)			(ppmv)	(ppmv)	Conversion			
										% SO2	% CS2	% COS	% CO
300	72.18	24.63	2.02	18.5	0.0	0.0325	1.44	0.0	0.0	100.0	#DIV/0!	97.1	97.8
240	72.18	24.65	2.02	7.9	0.0	0.0124	1.46	0.0	0.1	100.0	#DIV/0!	98.8	99.2
200	72.18	24.66	2.02	4.0	0.0	0.0056	1.46	0.0	0.9	100.0	#DIV/0!	99.4	99.6

Feed and equilibrium compositions reported on a dry & sulfur-free basis

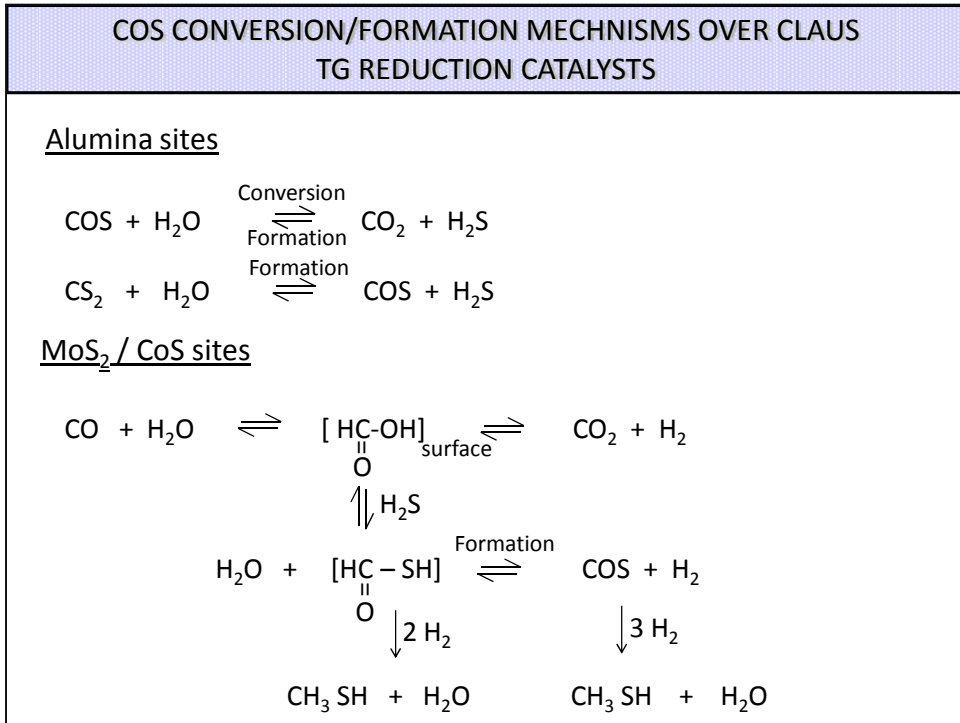[#] Wet feed composition also contained 800 ppmv of sulfur vapour (as S8).

Figure 6

COS FORMATION / CONVERSION CHEMISTRY

WGSR

$$CO + H_2O \xrightleftharpoons[\substack{Al_2O_3 \\ CoS/MoS_2}] [HC-OH] \xrightleftharpoons CO_2 + H_2$$

(with H_2S, $\delta+$ on HC, $O^{\delta-}$ double bonded)

$$[HC-SH] + H_2O$$

(with O double bonded to HC)

COS Formation:

$$CO + H_2S \longrightarrow \boxed{COS} + H_2 \quad (SGSR)$$

COS Conversion and Formation:

$$\boxed{COS} + H_2O \rightleftharpoons CO_2 + H_2S \qquad (COS\ hydrolysis)$$

Figure 7

COS CONVERSION/FORMATION MECHNISMS OVER CLAUS TG REDUCTION CATALYSTS

Alumina sites

$$CO S + H_2O \underset{Formation}{\overset{Conversion}{\rightleftharpoons}} CO_2 + H_2S$$

$$CS_2 + H_2O \overset{Formation}{\rightleftharpoons} COS + H_2S$$

MoS$_2$ / CoS sites

$$CO + H_2O \rightleftharpoons [HC\text{-}OH]_{surface} \rightleftharpoons CO_2 + H_2$$

(with O double bonded, H_2S vertical)

$$H_2O + [HC-SH] \overset{Formation}{\rightleftharpoons} COS + H_2$$

(with O double bonded)

$$\downarrow 2H_2 \qquad\qquad \downarrow 3H_2$$

$$CH_3SH + H_2O \qquad CH_3SH + H_2O$$

Methyl Mercaptan (CH_3SH) Formation in CRP Units

From time to time, operators report the formation of methyl mercaptan in CRP units demonstrating that the compound had not been present in the feed tail gas. Specifically, field analyses show that methyl mercaptan definitely arises in the hydrogenation reactor. This observation has been duplicated in our laboratories on several occasions and, indeed, is a feature of the present work (Table 1). From a synthesis viewpoint, methyl mercaptan is most likely to be formed from a compound that already contains a C-S bond making COS and CS_2 possible precursor molecules. CS_2 is the most likely candidate because hydrogenation of one of the C-S bonds will lead to methyl mercaptan through hydrogen addition and hydrogenolysis of one of the C-S bonds. A series of experiments in which CS_2 was excluded from the feed demonstrated that CS_2 is responsible for most of the methyl mercaptan produced over the catalyst used in this study (Table 3, Figure 8). Interestingly, methyl mercaptan formation was not zero in the absence of CS_2 but the bulk of it clearly arises by reduction of CS_2.

The temperature dependence seen (Figures 8 and 9) illustrates that the amount of mercaptan found in the product gas must depend on the ability of the catalyst to hydrogenate CS_2 all the way to CH_4 at lower temperatures. With the catalyst used in this work, even 300°C was insufficient to remove all methyl mercaptan with 240°C resulting in a greater residual level of mercaptan. At 200°C, this catalyst would appear to have only minimal activity to hydrogenate CS_2 as the amount of methyl mercaptan produced (Table 1) was similar to the low levels found in experiments in which no CS_2 was used. The correlation between mercaptan formation and CS_2 destruction is shown in Figure 10.

Why is methyl mercaptan observed in small amounts even when no CS_2 was present? Most likely, it can be formed by hydrogenation of COS but it could also be produced by hydrogenation of the thio-formic acid produced by interaction of H_2S with the intermediates of the WGSR (Figure 7). The commercial relevance of these observations is that it is important to destroy CS_2 in the first Claus catalytic converter so avoiding the possibility of its hydrogenation in the tail gas unit, but, the possibility of making methyl mercaptan in the hydrogenation unit, albeit in ppm levels, may always be present via WGSR intermediates. Interestingly, equilibrium calculations (Table 2a and b) reveal that methyl mercaptan is expected to be formed in very small amounts at low temperatures (200 - 240°C).

High efficiency, low temperature Claus tail gas reduction catalysts may, in fact, convert CS_2 completely by hydrogenation because < 240°C, the rate of CS_2 hydrolysis on alumina sites is likely insufficient to effect its complete removal. However, even with very effective low temperature catalysts, it is advisable to deal with CS_2 in the upstream first converter so strengthening the argument for the use of titania in the first converter for plants which require ultra-high sulfur recovery (> 99.95 %).

Table 3

Experimental Data and Calculated Conversions for the Co/Mo-Based Tail Gas Reduction Catalyst at 200 - 300°C and Space Velocity of 2000 h^{-1} - Cut CS$_2$

DRY FEED (saturated with 22% H2O)[#]

% N2	% CO2	% H2S	% COS	% SO2	% CO	%H2	% CS2	MeSH	H2S:SO2
72.18	23.09	0.755	0.064	0.378	1.51	1.92	-	-	2.00

			SAMPLE							Conversion		
Time(hrs): (300C)			(ppmv)	(ppmv)			(ppmv)	(ppmv)	% SO2	% CS2	% COS	% CO
1.0	72.18	25.04	1.66	218	4.9	0.191	1.96	1.5	1.6	99.9	-	65.9	87.3
2.0	72.18	25.07	1.67	213	4.4	0.192	1.95	1.4	2.6	99.9	-	66.7	87.3
4.0	72.18	25.50	1.71	212	3.5	0.185	2.08	1.2	3.2	99.9	-	66.8	87.7
6.0	72.18	25.18	1.70	204	3.5	0.180	2.06	1.1	3.2	99.9	-	68.1	88.1
8.0	72.18	25.50	1.72	202	2.6	0.180	2.03	1.1	2.8	99.9	-	68.5	88.1
(240C)												
9.0	72.18	24.27	1.59	552	17	0.458	1.77	1.4	6.9	99.6	-	13.7	69.7
10.0	72.18	24.55	1.59	705	12	0.452	1.69	1.4	8.2	99.7	-	-10.1	70.0
12.0	72.18	25.04	1.65	814	11	0.459	1.73	1.0	5.1	99.7	-	-27.2	69.6
14.0	72.18	24.49	1.62	877	24	0.453	1.64	0.8	5.8	99.4	-	-37.1	70.0
16.0	72.18	24.60	1.62	1006	21	0.460	1.68	1.1	6.4	99.4	-	-57.3	69.6
(200C)												
17.0	72.18	23.88	0.85	1656	55	0.960	1.66	1.0	3.7	98.5	-	-158.8	36.4
18.0	72.18	23.82	0.75	2539	200	1.044	1.65	0.9	3.3	94.7	-	-296.8	30.9
20.0	72.18	23.47	0.51	1707	414	1.122	1.61	0.6	1.4	89.1	-	-166.7	25.7
22.0	72.18	23.73	0.47	1592	449	1.301	1.69	0.7	1.6	88.1	-	-148.7	13.9
24.0	72.18	23.87	0.46	1566	477	1.314	1.68	0.6	1.3	87.4	-	-144.7	13.0

Feed and product analyses reported on a dry & sulfur-free basis

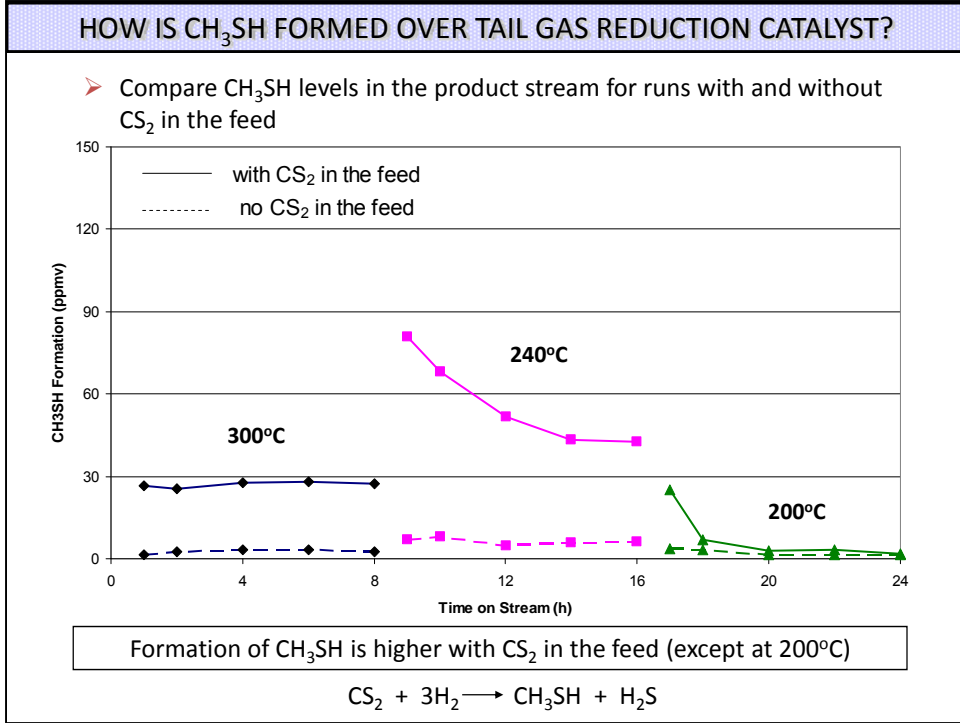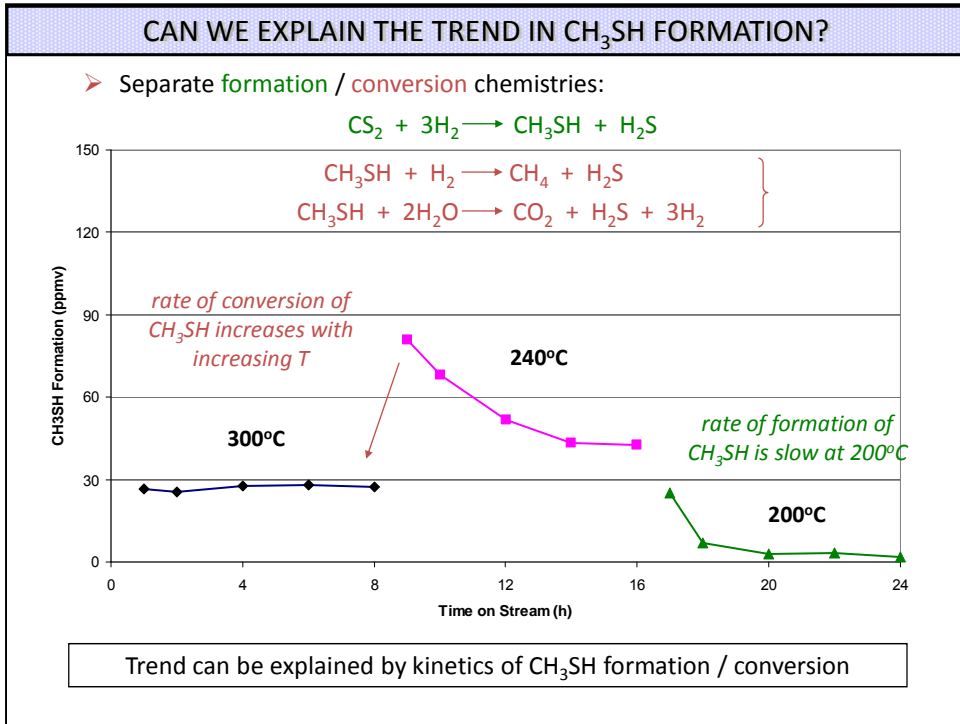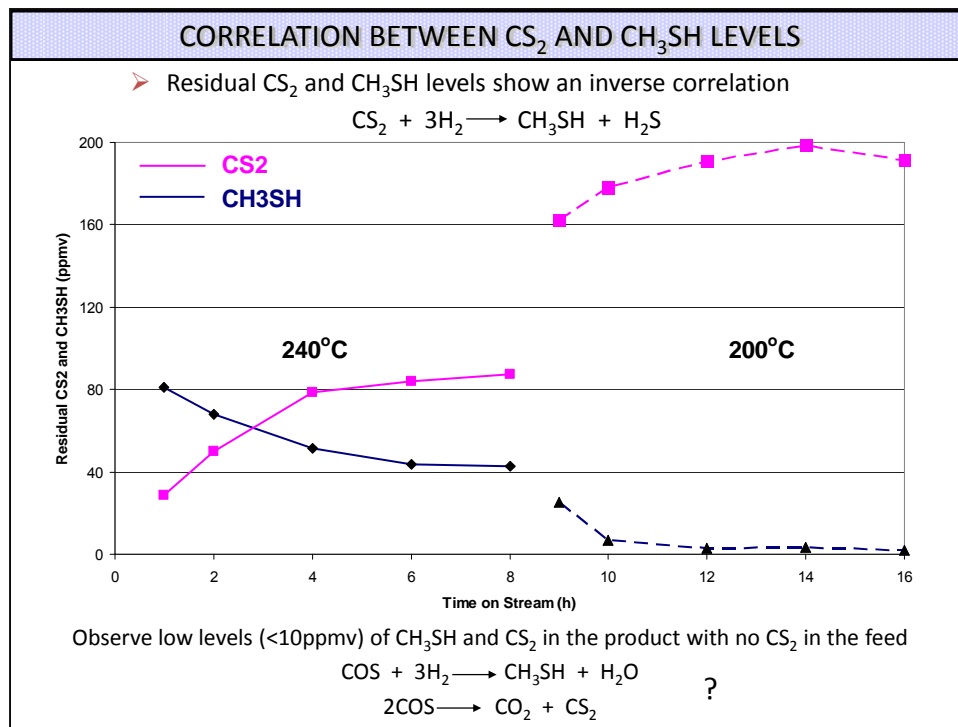[#] Wet feed composition also contained 800 ppmv of sulfur vapour (as S8).

Figure 8

HOW IS CH₃SH FORMED OVER TAIL GAS REDUCTION CATALYST?

➢ Compare CH$_3$SH levels in the product stream for runs with and without CS$_2$ in the feed

——— with CS$_2$ in the feed

- - - - - no CS$_2$ in the feed

(Y-axis: CH3SH Formation (ppmv); X-axis: Time on Stream (h))

300°C 240°C 200°C

Formation of CH$_3$SH is higher with CS$_2$ in the feed (except at 200°C)

$$CS_2 + 3H_2 \longrightarrow CH_3SH + H_2S$$

Figure 9

CAN WE EXPLAIN THE TREND IN CH₃SH FORMATION?

➢ Separate formation / conversion chemistries:

$$CS_2 + 3H_2 \longrightarrow CH_3SH + H_2S$$

$$CH_3SH + H_2 \longrightarrow CH_4 + H_2S$$

$$CH_3SH + 2H_2O \longrightarrow CO_2 + H_2S + 3H_2$$

rate of conversion of CH$_3$SH increases with increasing T

rate of formation of CH$_3$SH is slow at 200°C

300°C 240°C 200°C

(Y-axis: CH3SH Formation (ppmv); X-axis: Time on Stream (h))

Trend can be explained by kinetics of CH$_3$SH formation / conversion

Figure 10

CORRELATION BETWEEN CS$_2$ AND CH$_3$SH LEVELS

➤ Residual CS$_2$ and CH$_3$SH levels show an inverse correlation

$$CS_2 + 3H_2 \longrightarrow CH_3SH + H_2S$$

Observe low levels (<10ppmv) of CH$_3$SH and CS$_2$ in the product with no CS$_2$ in the feed

$$COS + 3H_2 \longrightarrow CH_3SH + H_2O$$
$$2COS \longrightarrow CO_2 + CS_2 \qquad ?$$

The Importance of Catalyst Activation to CO and CS$_2$ Conversion

Earlier it was noted that catalyst activation by treatment of the oxide form with H$_2$ and H$_2$S was important to obtain an effective tail gas catalyst. The chemistry that occurs during this procedure (Figure 11) not only results in conversion of the CoO and MoO$_3$ to the respective sulfides, but also it results in reduction of Mo from its + 6 oxidation state to the catalytically active + 4 species. Conceivably this reduction can be accomplished by both H$_2$S and H$_2$ but overall catalyst activity is improved when both are used during activation (Figure 11).

It could be argued that the Claus tail gas itself should be sufficient to activate the virgin catalyst as H$_2$S and H$_2$ are present so some activity experiments were conducted using catalyst that was activated in situ with Claus tail gas and also with material which was sulfided according to standard industrial procedures using an H$_2$S/H$_2$ mixture. Two sets of data were collected, one at 250°C and another at 300°C (Figures 12 and 13) with the experiments using the same catalyst samples. The data set at 250°C was collected first. This point is important because the results obtained at 300°C have used catalyst which has been subjected to Claus tail gas at 250°C for 32 hours and then was "sulfided" further when the experiments were carried out at 300°C.

Figure 11

ACTIVATION CHEMISTRY FOR CLAUS TAIL GAS REDUCTION CATALYSTS

$$Co^{II} O + H_2S \longrightarrow Co^{II} S + H_2O$$

$$Mo^{VI} O_3 + 3 H_2S \longrightarrow Mo^{IV} S_2 + \tfrac{1}{8} S_8 + 3 H_2O$$

$$Mo^{VI} O_3 + H_2 \longrightarrow Mo^{IV} O_2 + H_2O$$

$$Mo^{IV} O_2 + 2 H_2S \longrightarrow Mo^{IV} S_2 + 2 H_2O$$

Figure 12

COMPARISON BETWEEN SULFIDED AND NON-SULFIDED Co-Mo AT 250°C FOR TG RUN
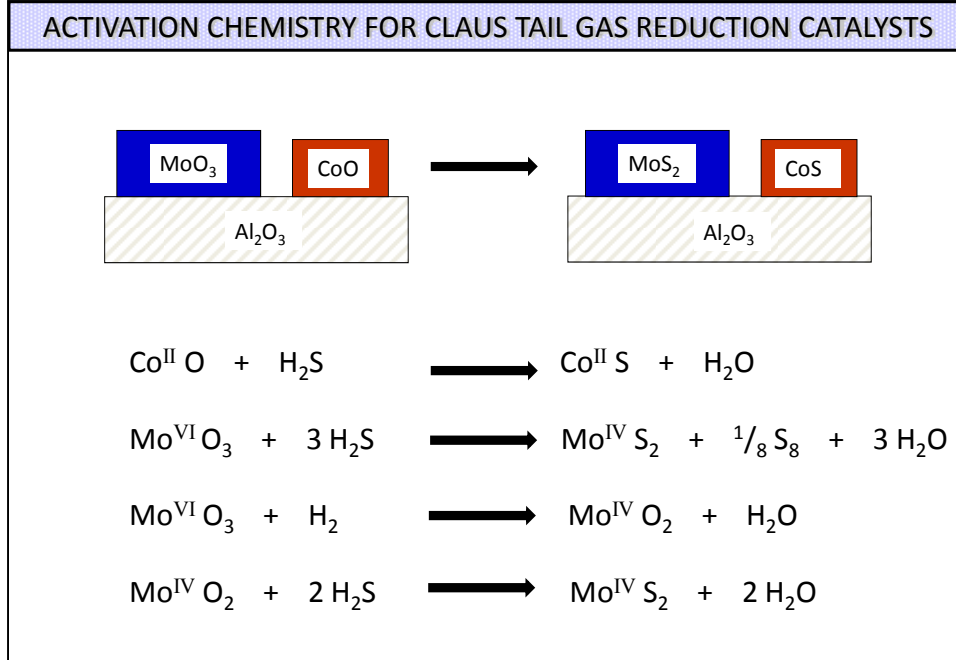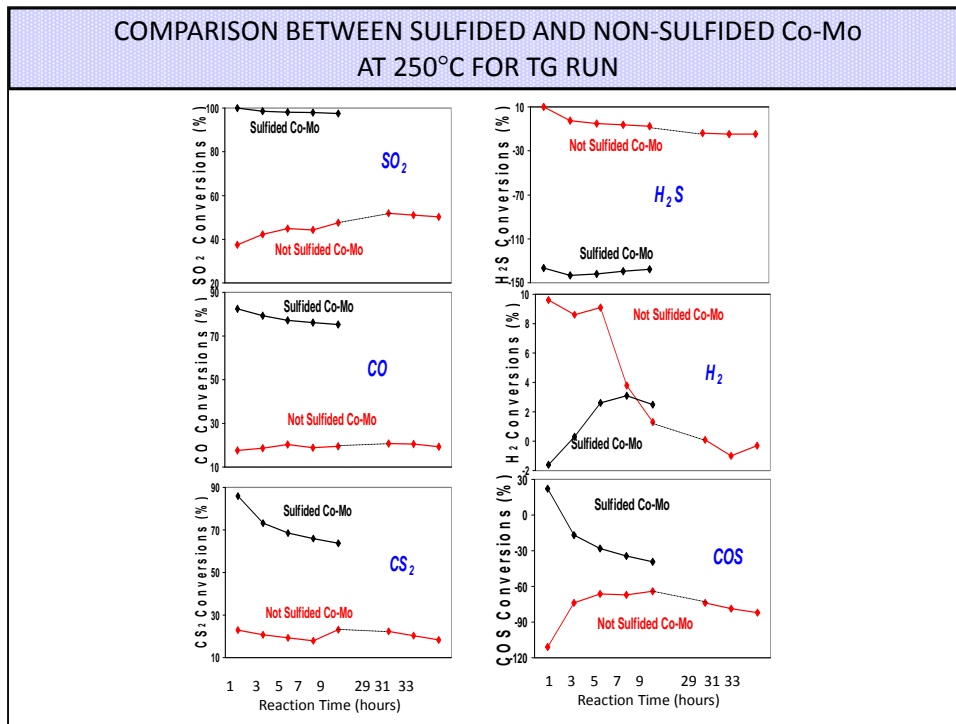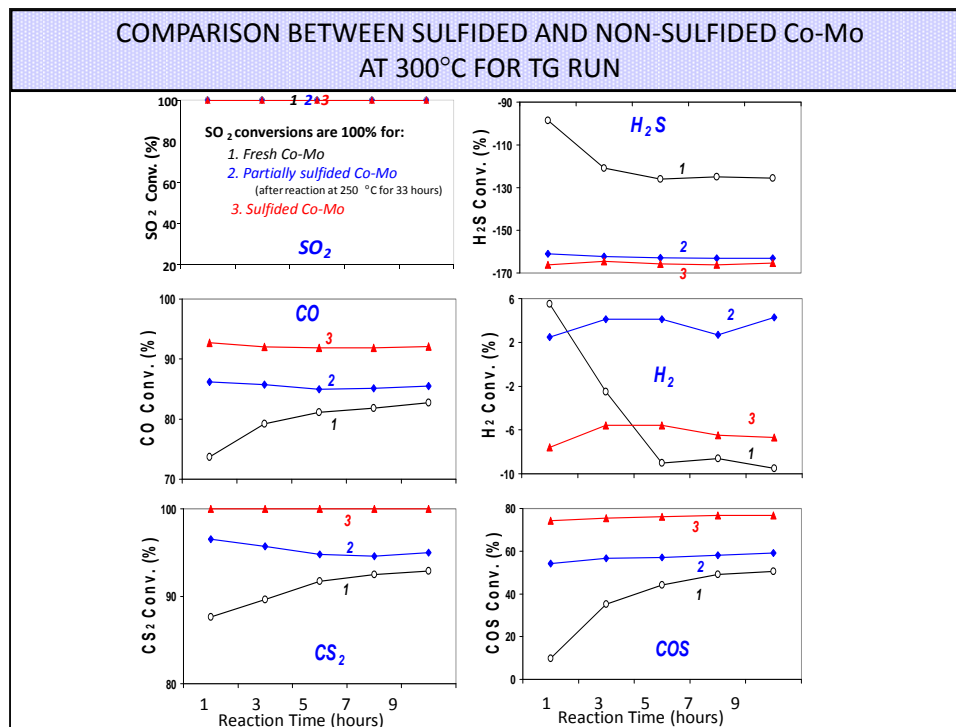
Figure 13

The first general conclusion from the data collected at 250°C (Figure 12) is that catalyst that has been pre-sulfided according to standard commercial procedures is more active for conversion of all tail gas species. In addition to improving SO_2 conversion (ca. 50 to 95 %), the H_2/H_2S treated catalyst is much more active for CO and CS_2 conversion with the conversion for CS_2 increasing from ca. 20 to 60 % for the H_2/H_2S sulfided catalyst. This observation underscores the conclusion that hydrogenation is the major conversion pathway for CS_2 at 250°C. Furthermore, at least for the catalyst used in these studies, the reducing potential of the CO is not available to any significant extent unless the catalyst is pre-sulfided. Trends in COS production/consumption are much more difficult to interpret for reasons already discussed.

The experiments conducted at 300°C include a third data set for new catalyst so that cumulative effect of in situ sulfidation at 250 and 300°C can be compared to the catalyst which had been pre-activated using a commercial procedure as well as to a virgin sample (Figure 13). For all species, conversions were greatest using the catalyst that had been pre-activated with H_2S and H_2 using a commercial procedure with the exception that SO_2 was readily reduced by all three catalysts. Interestingly, CS_2 conversion only reached 100 % for the H_2S/H_2 activated catalyst strongly suggesting that hydrogenation (or hydrolysis at MoS_2 sites) contribute to CS_2 conversion even at 300°C. Most probably, this is also the case for COS at 300°C as, again, highest conversion was obtained with

catalyst pre-activated with the commercial procedure. The take home message here is that the catalyst pre-activation is very important.

Effect of BTX on Claus Tail Gas reduction Catalysts

It is well known that Claus alumina and titania catalysts are deactivated by hydrocarbons, particularly the aromatics toluene and xylene at process temperatures > 300°C. Benzene is much less troublesome, likely because the mechanism of deactivation occurs through the methyl groups of toluene and xylene via carbocation intermediates (Figure 14). In practice, when BTX is present in Claus process gas, it is seen that the carbon content of alumina and titania increase with time on-stream, leading to occlusion of the pore structure of the catalyst and, consequently, impaired mass transfer. Most probably, a complex network polymer, carsul, consisting of aromatic species linked together by C-S bonds builds up on the catalyst surface. A key aspect of the mechanism shown in Figure 14 is that elemental sulfur, produced in the Claus reaction, is required to initiate carsul formation.

In a CRP process, BTX may be present in the process gas as a result of the original acid gas composition or in the fuel gas supplied to a RGG-re-heater unit. It can be argued that BTX should have little impact on the CRP catalyst as the generally reducing conditions should limit the presence of elemental sulfur and, so, eliminate the oxidative pathways that convert BTX to carsul. However, < 240°C, some sulfur was observed so, perhaps, presenting the opportunity for carsul formation. But, at this temperature and lower values, it is known that there is little interaction between BTX and sulfur on Claus catalysts. So, a general prediction is that low temperature CRP systems should not experience catalyst degradation due to BTX. An overall conclusion is that in low temperature CRP systems, hydrocarbons (BTX) should have little influence on catalytic activity because the temperature is too low and in standard units operating at 300°C, the absence of sulfur should preclude carsul formation. But, what if SO_2 reduction to H_2S always proceeds through initial formation of sulfur, even at 300°C?

Data obtained from a series of experiments conducted at 300°C with BTX added to the Claus tail gas feed show that some catalyst degradation might be expected with persistent influx of BTX as the carbon content did increase over an 81 hour period along with some surface area reduction (Figure 15). Two catalysts were investigated, one in which the catalyst was allowed to "sulfide" in situ under the influence of the process stream, and another which was activated by the commercial procedure. Regardless of these treatments carbon build up was observed and xylene was the most reactive component, as was observed in studies with alumina and titania Claus catalysts.

The build up of carbon on a reduction catalyst at 300°C is a very interesting observation since, although elemental sulfur is not observed as a product under these conditions, its
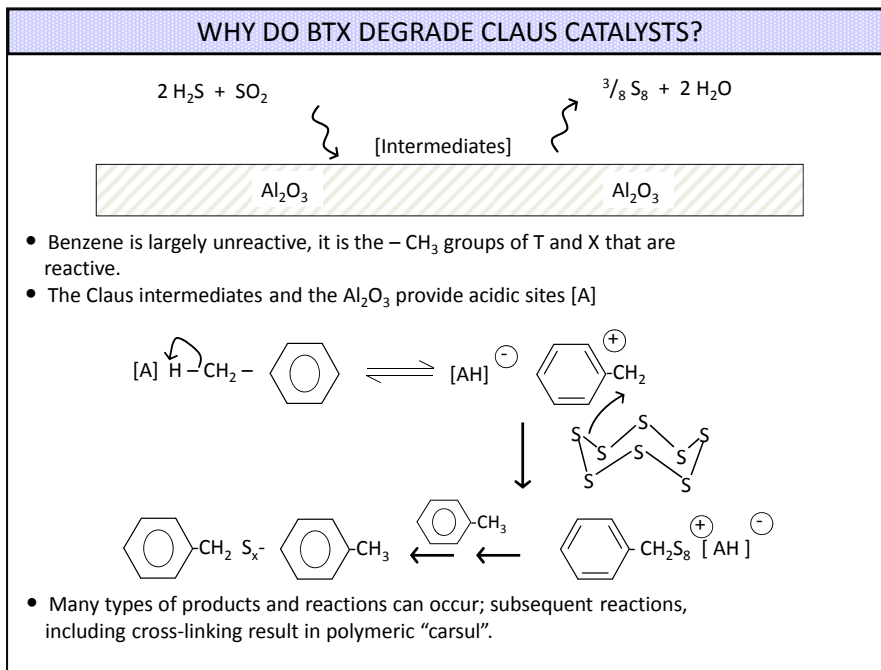
Figure 14

WHY DO BTX DEGRADE CLAUS CATALYSTS?

$2 H_2S + SO_2$ $^3/_8 S_8 + 2 H_2O$

[Intermediates]

Al_2O_3 Al_2O_3

- Benzene is largely unreactive, it is the $- CH_3$ groups of T and X that are reactive.
- The Claus intermediates and the Al_2O_3 provide acidic sites [A]

- Many types of products and reactions can occur; subsequent reactions, including cross-linking result in polymeric "carsul".

Figure 15

EFFECT OF BTX ON CLAUS REDUCTION TAIL GAS CATALYST

Overall:

- Conversion: As with Claus catalysts, xylene is the most reactive species but conversion is low (5 – 10%)

- Experiments conducted over 14 – 81 h. show some carbon (C) build up on the catalyst.

Catalyst	SA ($m^2.g^{-1}$)	%C	%H
1. Fresh catalyst	204	0.1	0.95
2. Sulfided by Claus TG, BTX (119ppmw) for 14 h. at 300°C	185	0.32	0.78
3. Pre-sulfided, BTX at 300°C, 81 h.	180	0.37	0.68

- The amount of C formed is less than on Claus catalysts

formation as an intermediate of SO_2 reduction suggests a reaction pathway in which sulfur is first formed via the Claus reaction and then reduced to H_2S at an active MoS_2 site. If this suggestion is true at 300°C, it is more likely to be the "real" mechanism at 240°C or lower temperatures but at 240°C and below, interaction between aromatics and sulfur is likely to be too slow to cause catalyst degradation. Of course, the removal of the RGG in low temperature units greatly reduces the possibility of hydrocarbons ingress into the catalytic reactor.

Conclusions

Studies on the reaction pathways of Claus tail gas reduction catalysts indicate the following:

1. Reduction of SO_2 occurs via sulfur formed in the Claus reaction with H_2S over either alumina or MoS_2 sites or by partial reduction of SO_2 at MoS_2 followed by further reduction with H_2 to H_2S. Sulfur formation can be observed experimentally < 240°C. **Commercial implication: There is more than one way to clog your quench tower with sulfur.**

2. The WGSR requires MoS_2 sites that have been produced by activation of the catalyst with H_2/H_2S mixtures as recommended by suppliers for their individual catalysts. **Commercial implication: new catalyst activity will be dependent on how rigorously the catalyst is pre-treated.**

3. COS conversion may be limited by formation from either CO or from CO_2 by interaction of H_2S with surface intermediates of the WGSR. Net COS production might be seen at temperatures < 250°C, an observation that is probably linked to the time on-stream and activity of the catalyst. **Commercial implication: plants requiring very high sulfur recovery (> 99.95 %) should monitor COS levels.**

4. CS_2 and, probably, COS conversion occurs principally on reduction sites and not by hydrolysis. Hydrogenation of CS_2 proceeds via methyl mercaptan and, finally to methane. **Commercial implication: Conditions for the first Claus catalytic converter should be such as to destroy as much CS_2 as possible to avoid methyl mercaptan formation in the CRP unit.**

5. Hydrocarbons such as toluene and xylene can degrade Claus tail gas reduction catalysts particularly for high temperature units, probably because of intermediate sulfur formation during SO_2 reduction. **Commercial implication: Keep reactive hydrocarbons out of CRP hydrogenation units.**

The chemistry of Claus tail gas catalysis is summarized in Figures 16 and 17.
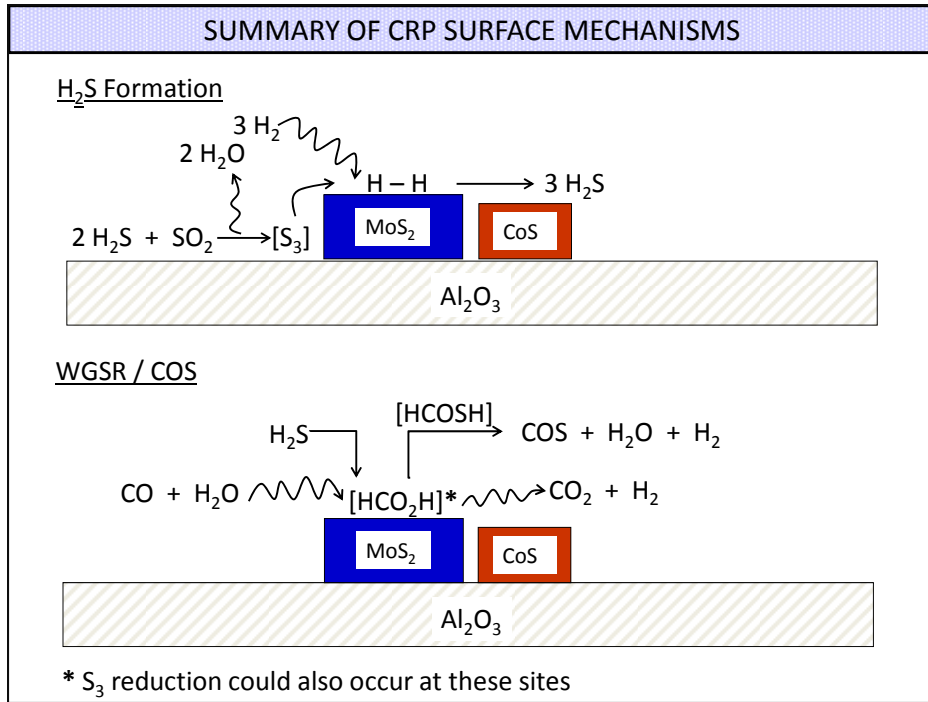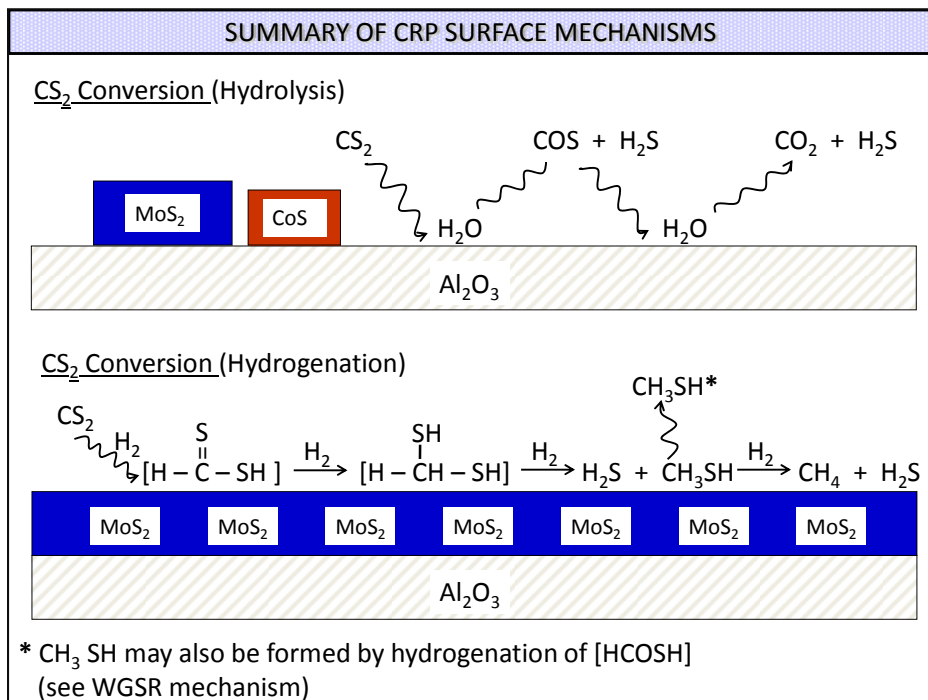
Figure 16

SUMMARY OF CRP SURFACE MECHANISMS

H$_2$S Formation

WGSR / COS

* S$_3$ reduction could also occur at these sites

Figure 17

SUMMARY OF CRP SURFACE MECHANISMS

CS$_2$ Conversion (Hydrolysis)

CS$_2$ Conversion (Hydrogenation)

* CH$_3$ SH may also be formed by hydrogenation of [HCOSH]
(see WGSR mechanism)