Conversion of CS$_2$ and COS over alumina and titania under Claus process conditions: reaction with H$_2$O and SO$_2$

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Abstract

Catalytic conversion of CS$_2$ in the Claus process using either alumina or titania has always been assumed to proceed via hydrolysis. Although this conclusion is supported by the results of this study, data reported here show that the high CS$_2$ conversion activity of titania may be due, in part, to the reaction of CS$_2$ with SO$_2$, a process which proceeds almost quantitatively at 320°C. This reaction was also shown to have an appreciable rate at 250°C, suggesting that some of the CS$_2$ conversion activity of titania at second Claus converter conditions may be due to reaction with SO$_2$. COS was identified as an intermediate product of the reaction of CS$_2$ with SO$_2$. Although these studies confirmed that alumina promotes hydrolysis of CS$_2$, the industrial observation that it is not as efficient a catalyst as titania for the conversion of CS$_2$ may be due to the limited ability of alumina to promote reaction of CS$_2$ with SO$_2$. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: CS$_2$; COS conversion; Alumina; Titania

1. Introduction

The Claus process is utilized worldwide for the conversion of H$_2$S to elemental sulfur [1]. It consists of a high temperature partial combustion stage and a series of catalytic stages for conversion of residual H$_2$S and SO$_2$ formed in the thermal stage. CS$_2$ is formed in the thermal stage when hydrocarbon impurities enter the system with the acid gas [1] and, unless converted in the catalytic stages, it results in emissions to the atmosphere when the tail gas is passed through an incinerator. Generally, it is accepted that titania is a more effective catalyst for conversion of CS$_2$ than alumina under Claus process conditions with alumina catalysts being particularly unreactive at temperatures less than 300°C [2]. Consequently, in Claus plants producing considerable quantities of CS$_2$ in the furnace stage, titania is used most often in the first converter.

Generally, it is assumed that CS$_2$ is converted by hydrolysis over both alumina and titania [2] although not much work has been published to explain the high CS$_2$ conversion activity of titania. A recent paper attributes the high activity of titania to its ability to resist sulfation [3]. An interesting study by Lavalley and co-workers showed [4] that α-alumina was, in fact, more active than titania (anatase) when neither H$_2$S or SO$_2$ were present in the feed gas but that titania was considerably more active when both H$_2$S and SO$_2$ were present along with traces of O$_2$. These workers had included O$_2$ in the feed to mimic commercial Claus conditions since it is believed that O$_2$ is either carried over from the main burner in the furnace or

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results from inefficient combustion in direct re-heaters upstream of the catalyst reactors. A key finding of the Lavalley study [4] was the observation that when O2 was present, sulfate was formed on both titania and alumina. The higher activity of titania was ascribed to the more facile reduction of sulfate by H2S to produce a lower steady-state sulfate concentration.

It is interesting to note that many papers in the literature link sulfate formation to loss of Claus catalyst activity but the data supporting this assertion are indirect in nature. Recent work in our laboratories [5] has shown that sulfate formation does not affect conversion of H2S and SO2 to sulfur over alumina but that it does decrease conversion of CS2. Moreover, we have shown that sulfate is formed on alumina as a result of the Claus reaction when no O2 was present in the system. This observation may well explain the experiments of Lavalley and co-workers [4] which showed that alumina is, in fact, more active for hydrolysis of CS2 than titania when no H2S and SO2 (the agents for sulfate formation) are present, since under this condition, no sulfate can be formed.

Work in our laboratories on the chemistry of the Claus furnace has shown that CS2 is converted by both H2O and by SO2 at temperatures exceeding 900°C. Although details of these high temperature reactions have been unraveled only partially [1], the product distribution allows the following overall reactions to be written:

\[
\begin{align*}
\text{CS}_2 + 2\text{H}_2\text{O} & \rightarrow 2\text{H}_2\text{S} + \text{CO}_2 \quad (1) \\
\text{CS}_2 + \text{SO}_2 & \rightarrow \frac{3}{2}\text{S}_2 + \text{CO}_2 \quad (2)
\end{align*}
\]

It has been assumed that reaction (1) is responsible for the catalytic conversion of CS2 in the Claus process over both alumina and titania and many laboratory studies have proven that it proceeds readily [2–4] above 300°C. Since reaction (2) could also occur catalytically, it was of interest to determine if this process makes any contribution to the conversion of CS2 over either alumina or titania. A review of the literature shows that this reaction has not been studied although work by Dalla Lana and co-workers [6] has shown that COS can be converted by SO2 over alumina but that the reactive sites for this process were readily poisoned by CO2. Lavalley and co-workers suggest that COS is an intermediate in the catalytic conversion of CS2 by water over alumina [3,4] making it possible that COS formed as an intermediate in CS2 conversion is converted further by reaction with SO2. In this study, we report the catalytic conversion of CS2 and COS by both H2O and SO2 over alumina and titania and show that conversion of CS2 and COS by SO2 are especially facile reactions over titania.

2. Experimental procedures

Commercially available samples of unpromoted alumina and titania (anatase) Claus catalysts, supplied by Procatalyse (Paris, France) were used in all of the experiments in the form of 4–5 mm balls or extrudate. The surface areas of the fresh catalysts were measured on an Advanced Scientific Designs RXM-100 surface characterization system and gave values of 356 and 119 m2/g, respectively for the alumina and titania samples. These forms were directly loaded into a vertical stainless steel fixed-bed reactor of dimensions 2.5 cm o.d. × 39.4 cm length with an internal diameter of 2.1 cm. The temperature of this reactor was isothermally controlled to within ±1°C over its entire length by an ebullated sand-bath and monitored through a series of axially located thermocouples.

Delivery of the feed gases to the reactor was controlled by means of mass flow controllers except for CS2 and H2O, which were introduced through a syringe pump and saturator, respectively. Removal of any elemental sulfur formed during a reaction was handled by condensation in suitable traps and dried sulfur-free samples of the product gas were retrieved for GC analysis.

Chromatography of the various species (CO2, H2S, COS, SO2 and CS2) was performed on a Chromosorb 105 column using helium as the carrier gas and a thermal conductivity detector. Percent conversion of the CS2 due to reaction was calculated as follows:

\[
\text{Conversion} (\%) = \frac{(\text{CS}_2)_{\text{feed}} - \{(\text{CS}_2)_{\text{prod}} \times (N_2)_{\text{feed}} / (N_2)_{\text{prod}}\}}{(\text{CS}_2)_{\text{feed}}} \times 100
\]

where \((\text{O}_{\text{feed}})\) and \((\text{O}_{\text{prod}})\) correspond to the mole% concentration of CS2 or N2 in the feed and product streams. This method of calculating the conversion of CS2 uses the inert N2 as a tie component correcting
for molar changes in the product stream due to either reaction or removal of condensables.

Feed gases with compositions of 1.3 mole% CS₂ and 30 mole% H₂O or SO₂, and balance N₂, were initially studied. The activity of the catalyst was monitored over a period of 4–5 h in individual experiments using reactor temperatures of 330 and 250°C and space velocities of 1000–200 h⁻¹.

3. Results and discussion

3.1. Conversion of CS₂ over alumina at 330°C

Data plotted in Fig. 1 show that CS₂ is readily hydrolyzed over alumina at typical Claus first converter conditions (space velocity of 1000 h⁻¹) but that relatively little conversion occurred when SO₂ was used in place of H₂O. It is interesting that an initially moderate CS₂ conversion by SO₂ (ca. 35%) fell to ca. 10% within 3 h on-line. In both experiments, an excess of either H₂O or SO₂ was used relative to CS₂ to mimic, approximately, the ratios found in commercial reactors. Although alumina has a low activity for conversion of CS₂ by SO₂ at a space velocity of 1000 h⁻¹, a substantially higher initial conversion (ca. 80%) was observed at the lower space velocity of 200 h⁻¹ (Fig. 1). However, even at this lower space velocity, loss of activity to ca. 55% conversion was observed over the 3 h duration of these experiments. Given these results, it can be concluded that CS₂ conversion over alumina is much more likely to occur in commercial systems by reaction with H₂O, especially as H₂O is present in a roughly 10-fold excess compared to SO₂.

3.2. Conversion of CS₂ over titania at 330°C

As is clear from the data shown in Fig. 2, CS₂ is effectively converted over titania by both H₂O and SO₂. When using SO₂, conversions in excess of 96% were observed although reaction with H₂O yielded the highest conversion (>99%) at 1000 h⁻¹ space velocity. With either H₂O or SO₂ as reactants, no evidence for a decrease in conversion was observed over the period of the experiment (4 h). The conversion of CS₂ by SO₂ over titania does exhibit some kinetic limitation at 1000 h⁻¹ as on decreasing the space velocity to 200 h⁻¹, the CS₂ conversion increased to >99% from 96% at 1000 h⁻¹ (Fig. 2). Note that free energy minimization shows that neither hydrolysis of CS₂ or its conversion by SO₂ are equilibrium limited under the reaction conditions used in this study.

Overall, it can be concluded that the high activity of titania catalysts for CS₂ conversion at first converter conditions can be attributed to reaction with both H₂O and SO₂. The contribution of each reaction in a
3.3. \textit{CS}_2 \textit{conversion over titania by H}_2\textit{O and SO}_2 \textit{at 250°C}

It is well known that \textit{CS}_2 \textit{conversion over alumina at second converter conditions (ca. 250°C)} is very low (<10%) [2]. Thus, it is of interest to determine the relative efficiency of the \textit{CS}_2 \textit{conversion over titania by either H}_2\textit{O or SO}_2 \textit{at second converter conditions}. These experiments (Fig. 3) showed that the rate of hydrolysis of \textit{CS}_2 \textit{over titania is still very high (>95%) but that reaction with SO}_2, although substantial, is much less effective (ca. 40% conversion after 4 h on-line). The observation of COS in the \textit{CS}_2/\textit{SO}_2 experiment (see Fig. 3) is interesting in that it parallels the mechanism for the hydrolytic conversion of \textit{CS}_2 \textit{over alumina although, for the SO}_2 \textit{reaction, it is necessary to postulate S}_2\text{O as an intermediate:}

\[
\text{CS}_2 + \text{SO}_2 \rightarrow \text{COS} + [\text{S}_2\text{O}] \rightarrow \text{CO}_2 + \frac{3}{8}\text{S}_8
\]

\text{S}_2\text{O would be a very reactive species in this system being consumed either by the COS, as shown, or by reaction with another molecule of CS}_2.

Overall, these data show that titania is a very effective catalyst for conversion of \textit{CS}_2 \textit{by H}_2\textit{O at second converter temperatures and that significant conversion is possible via SO}_2. However, as suggested earlier, the relative importance of each reaction at second converter temperatures may be controlled by the competitive adsorption of either \textit{H}_2\textit{O or SO}_2 and, perhaps, \textit{CS}_2 on the titania surface.

3.4. \textit{Conversion of COS by SO}_2 \textit{over alumina and titania}

\text{COS, as well as being an intermediate product in the conversion of CS}_2, is also formed in the Claus thermal stage by reaction of either \textit{H}_2\textit{S with CO}_2 or of \textit{CO}_2 with \textit{S}_2 [1]. If unconverted in the catalytic units, it may also contribute to the emissions from a Claus plant. Consequently, its conversion in the catalytic units is also of some importance. Generally, very high conversion of \textit{COS over alumina is observed and it has always been assumed that the conversion occurs by
hydrolysis [2–4, 6], notwithstanding the data already published by Dalla Lana and co-workers on the conversion of COS by SO₂ over alumina [6]. In order to determine whether reaction of COS with SO₂ makes any contribution to the overall conversion observed in the field, a series of experiments was conducted to ascertain the reactivity of COS towards SO₂ over both alumina and titania.

As may be seen from Fig. 4, initial conversion of COS by SO₂ over alumina at 330°C was high using fresh catalyst (ca. 90%) but it decreased to ca. 60% after only 4 h on-stream. Since the trend in reduction of conversion is still downward at 4 h, it is probable that much lower steady-state conversions would be observed in a commercial catalytic converter. At 250°C very little conversion of COS by SO₂ over alumina was observed suggesting that this reaction would be of minimal importance in the second catalytic converter. Overall, these results parallel those obtained by Dalla Lana and co-workers [6] who suggested that the loss
of activity of alumina to promote the COS/SO\textsubscript{2} reaction was a result of adsorption of CO\textsubscript{2} onto the active sites. In contrast, quantitative COS conversion was observed over titania at 330°C. Also, although a high initial conversion of COS by SO\textsubscript{2} over titania was observed at 250°C (>90%, see Fig. 4), over a 4 h period the conversion dropped to ca. 60%.

In general, these results suggest that COS is readily converted over titania by SO\textsubscript{2} and that conversion over alumina by this reaction is less effective. However, the presence of large quantities of H\textsubscript{2}O in a commercial process gas makes it much more difficult to ascertain the mechanistic pathways of COS conversion and, since it is well known that COS is readily hydrolyzed over both alumina and titania, the actual mechanism of conversion over either catalyst will depend on the relative adsorption of the various reacting species.

4. Concluding comments

It has been demonstrated that the high activity of titania for the conversion of CS\textsubscript{2} in a Claus converter may be due to reaction with both H\textsubscript{2}O and SO\textsubscript{2}. This is the first observation of a catalytic CS\textsubscript{2}/SO\textsubscript{2} reaction. Although this process proceeds readily over titania at 320°C giving almost quantitative conversion over prolonged periods at commercial space velocities, alumina gives only moderate initial activity for conversion of CS\textsubscript{2} by SO\textsubscript{2} and becomes almost completely inactive after 4 h on-stream. Experiments at lower temperatures (250°C) revealed that COS was an intermediate product from the reaction of CS\textsubscript{2} with SO\textsubscript{2} over titania. Other experiments showed that COS reacts readily with SO\textsubscript{2} over titania inferring that the reaction of SO\textsubscript{2} with CS\textsubscript{2} and COS could be important processes for the conversion of these compounds in commercial reactors using titania.

Future work is addressing the effect of sulfate formation on CS\textsubscript{2} conversion over alumina and the role of sulfate in H\textsubscript{2}S/SO\textsubscript{2} conversion.

References
